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## ANALYTICAL ABSTRACTS

## 1.—GENERAL ANALYTICAL CHEMISTRY

*General reviews of progress, reagents and methods of general application.*

**4090. Reports on analytical methods.** U.K.A.E.A. Production Group, Operations Branch, Windscale.—The following reports have been issued by U.K.A.E.A., Risley, Warrington, Lancs. Detailed descriptions of the analytical methods are given. **Analytical methods for the inspection of ammonium nitrate**, PG Report 91 (W), 22 pp. **Analytical methods for the inspection of oxalic acid**, PG Report 92 (W), 16 pp. **Determination of plutonium in uranium plant solutions**, PG Report 95 (W), 6 pp. **Determination of caesium-137 in urine**, PG Report 98 (W), 9 pp. **Determination of strontium-89 and strontium-90 in urine**, PG Report 99(W), 14 pp. **Determination of  $\beta$ -activity (transmitted through a total absorber thickness of 5 mg of aluminium per sq. cm) in plant solutions containing plutonium**, PG Report 100(W), 6 pp. **Assay of urea**, PG Report 103(W), 4 pp. **Methods for the concentration of impurities from Windscale raw materials prior to spectrographic analysis by the iron flux technique**, PG Report 104 (W), 6 pp. **Spectrographic analysis of impurities in sodium dichromate**, PG Report 113(W), 9 pp. **Spectrographic determination of impurities in potassium bromide and bromate and sodium nitrite by direct excitation**, PG Report 115(W), 7 pp. **Inspection of tributyl phosphate**, PG Report 116(W), 15 pp.

**4091. Bibliography on analytical flame spectroscopy. 1956 to March 1959. III.** R. Mavrodineanu (Boyce Thompson Inst. for Plant Res., Inc., Yonkers, N.Y., U.S.A.). *Appl. Spectroscopy*, 1960, **14** (1), 17–23.—A further 196 references is given. (Cf. *Anal. Abstr.*, 1960, **7**, 2589.) P. T. BEALE

**4092. Analysis for industry.** A. M. G. Macdonald. *Ind. Chem.*, 1960, **36**, 88–90.—The determination of P by the molybdenum blue method with inorganic reducing agents is specially discussed. It is considered that hydrazine gives the most satisfactory results. (31 references.) S.C.I. ABSTR.

**4093. Method for obtaining weighed micro samples of moisture- or oxygen-sensitive compounds.** A. F. Williams and T. O. Park (Res. Dept., Nobel Div., I.C.I. Ltd., Stevenston, Ayrshire, Gt. Britain). *Analyst*, 1960, **85**, 126–130.—The apparatus described is a commercially available glove-box modified to form a nitrogen dry box in which the whole of the sampling is carried out and the tube is electrically sealed. A. O. JONES

**4094. Solochrome green V as a new analytical reagent.** A. M. Amin, H. Khalifa and A. S. Moustafa (Nat. Res. Centre, Dokki, Cairo, Egypt). *Z. anal. Chem.*, 1960, **173** (2), 138–148 (in English).—Solochrome green V (C.I. Mordant Green 15)

is useful as indicator in the titration of Zn and Mn with EDTA and as a colorimetric reagent for Zn at pH 11. The Zn complex has its absorption max. at 560 m $\mu$ , but photometric measurements are made at 660 m $\mu$  where the most accurate results are obtained. The accuracy for 3 to 15  $\mu$ g of Zn is within  $\pm 3\%$ . J. P. STERN

**4095. Analytical applications of organoselenium compounds. A study of chlorophenoselenazine.** F. Mateo López (Univ. of Laguna, Tenerife). Thesis, Univ. of Laguna, 1960, 87 pp.—The preparation of chlorophenoselenazine,  $C_{12}H_8NSeCl_2$  (I) by reaction of  $SeCl_4$  with diphenylamine is described. I is soluble in most organic solvents and crystallises from benzene as yellow plates, m.p. 210°. A 0.1% soln. of I in acetone or ethanol is turned green by oxidising agents such as  $KMnO_4$  and  $FeCl_3$ , but is not suitable for use as a redox indicator. The reaction of I with  $Pd^{4+}$  in acid soln. to form a violet complex  $(C_{12}H_8NSeCl_2)_2PdCl_2$  is specific and sensitive; the limit of identification is 4  $\mu$ g of Pd per ml. The dissociation constant of the complex is  $2.0$  to  $3.6 \times 10^{-4}$ . The presence of  $H_2O$  effects the wavelength of max. absorption and so should be kept to a minimum. Coloured ions such as  $Cu^{2+}$ ,  $Co^{2+}$  and  $Ni^{2+}$  interfere. G. H. FOXLEY

**4096. Pyromellite indicators. I. Acid-base indicators containing four condensed phenolic groups.** J. A. Bishop (Newark College of Engineering, N.J., U.S.A.). *Anal. Chim. Acta*, 1960, **22** (2), 117–119.—The pH of the colour change of six compounds formed by the condensation of phenols with pyromellitic anhydride has been investigated. E. G. CUMMINS

**4097. Ion-exchange resin indicators.** L. Légrádi (Veszprémmegyei Fésztégyár, Fűzőgyártelep, Hungary). *Magyar Kém. Foly.*, 1960, **66** (2), 76–79.—Several new ion-exchange indicators were prepared. For the titration of strong acids a strongly basic anion-exchange resin was used which contained bromophenol blue, cresol red or bromocresol purple as indicator. Strong bases and also pyridine were titrated in the presence of a cation-exchange resin of the sulphonic acid type containing o-ethylphenyl-4-azonaphthylamine hydrochloride, which is a new acid-base indicator in the pH range 2.6 to 4. A universal indicator soln. was also prepared; on anion-exchange resin, it can be used in the titration of strong acids, and on a cationic resin it can be used in the determination of a strong base. Besides these uses, the universal resin can be used for the determination of the pH of soln. The colours of the resin indicators often differ from those of the indicator in soln. A. G. PETO

**4098. Hydron II—A new indicator for the complexometric determination of calcium in the presence of magnesium.** I. S. Mustafin and E. S. Kruchkova (N. G. Chernyshevsky Saratov State Univ.). *Zhur. Anal. Khim.*, 1960, **15** (1), 20–23.—A screened

indicator is suggested for the determination of calcium hardness in weakly mineralised waters (5  $\mu\text{g}$ -equiv. per litre) in the presence of Mg. This indicator, Hydron II, is prepared by mixing one part of Acid Chrome dark green J (0.5% aq. soln.) with two parts of naphthol yellow (0.25% aq. soln.). There is interference from  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Mn}^{2+}$ , but not from  $< 1 \text{ mg}$  of Fe per litre. *Procedure*—To 50 ml of test soln. add 2 ml of N NaOH and 4 to 5 drops of Hydron II (an excess of indicator masks the colour transition). The soln. is titrated with EDTA (0.02 to 0.002 N) from bright pink to green. The indicator enables Ca to be determined in the presence of 100 times as much Mg.

A. BURWOOD-SMITH

**4099. Modification of the Bruhns method for the standardisation of alkali hydroxide solutions.** F. Čižka, L. Novotný and Z. Vojta (Dept. for Special and Phys. Anal. Methods, Inst. Chem. Technol., Prague). *Coll. Czech. Chem. Commun.*, 1960, **25** (2), 597-600 (in German).—The oxalic acid method of Bruhns (*Z. anal. Chem.*, 1906, **45**, 573; 1916, **55**, 23, 321) has been modified to overcome interference by the  $\text{CO}_3^{2-}$  present in the soln. *Procedure*—Oxalic acid soln. (0.05 to 0.5 N) (25 ml) is titrated with NaOH soln. to a pink-orange end-point, with methyl red as indicator. It is then treated dropwise at the boiling-point with 0.5 to 1 M  $\text{CaCl}_2$  (10 ml) and back-titrated to a yellow end-point. The results for NaOH soln. containing known amounts of  $\text{Na}_2\text{CO}_3$  are compared with those by the method of Treadwell (*Kurzes Lehrb. d. anal. Chem.*, 11th Ed., Wien, 1946, Vol. II, p. 478). The method can be applied to industrial lyes and alkali carbonates.

J. ZÝKA

**4100. Some theoretical considerations in analytical chemistry. IV. A method of calculating asymmetrical titration curves avoiding the use of cubic equations.** E. Bishop (Washington Singer Lab., Univ., Exeter, England). *Anal. Chim. Acta*, 1960, **22** (2), 101-105.—It is shown that the necessary precision in these calculations is more easily attained by the calculation of the volume which represents the difference from 100% reaction rather than by considering the total titrant volume. The point at which it becomes necessary to take account of the dissociation of the unsymmetrical reaction product is defined by a discriminant for a given maximum permissible relative error, and equations covering the curve on both sides of this point are given.

E. G. CUMMINS

**4101. Voltammetry of the system hydrogen-perchloric acid at a platinised platinum electrode. Coulometric preparation of a solution of perchloric acid in anhydrous methyl cyanide.** J. Vedel and B. Trémillon (École de Physique et de Chimie, Paris, France). *J. Electroanal. Chem.*, 1960, **1** (3), 241-247 (in French).—A standard soln. of  $\text{HClO}_4$  in anhyd. methyl cyanide may be prepared by oxidation of hydrogen in a 0.1 M  $\text{NaClO}_4$  soln. at a platinised platinum anode.

A. R. ROGERS

**4102. Dielectric measurements for structure determination and quantitative analysis.** F. Oehme (Inst. zur Entwicklung chem.-phys. Analysenmethoden, Weilheim/Obb.). *J. Electroanal. Chem.*, 1960, **1** (3), 181-204 (in German).—A review is presented, with 87 references. For quant. analysis, the "quasi-static" dielectric constant should be measured, at a frequency of  $< 1$  megacycle per sec. The apparatus and technique of measurement are briefly described. An important application is to

the determination of water in a wide variety of samples.

A. R. ROGERS

**4103. Oscillographic polarography.** G. F. Reynolds (Min. of Supply, Woolwich, London). *Z. anal. Chem.*, 1960, **173** (1), 65-69 (in English).—An outline of the basic principles of oscillographic polarography is given.

T. R. ANDREW

**4104. The application of polarography in industrial practice.** W. Büchler (CIBA A.-G., Basle, Switzerland). *Z. anal. Chem.*, 1960, **173** (1), 17-21 (in German).—Procedures are described for the polarographic determination of Cu and Pb in organic substances, after dissolution of the ash in  $\text{HCl}$ ; Mo in steel in an  $\text{HCl}$ -ammonium citrate basal soln.; methyltestosterone, 6-hydroxymethyltestosterone and 6-dehydromethyltestosterone when present together, in a basal soln. of 0.1 M tetramethylammonium chloride in 50% ethanol. The use of a S.C.E. and close control of the thermostat is recommended when using the cathode-ray polarograph.

T. R. ANDREW

**4105. Functions of errors in the method of determination by isotopic dilution.** P. Lebreton (Lab. de Chim. Biol., 93 rue Pasteur, Lyon, France). *Bull. Soc. Chim. France*, 1960, (1), 179-181.—The relative errors in a determination by isotopic dilution are theoretically related to the percentage counting error ( $200/\sqrt{N}$  for 96% limits where  $N$  is the number of counts), and the advantage of counting to a pre-determined time, or to a pre-determined number of counts is considered. In the pre-determined time method it is shown that the relative error is a minimum when the amount of added isotope is half the amount of inactive material to be measured. An experimental comparison of the two techniques is made. It is found that errors are  $\approx 5\%$  in the range in which the sample wt. is from 0.2 to 2 times the wt. of active isotope.

E. J. H. BIRCH

**4106. Activation analysis.** A. H. W. Aten, jun. (Inst. Kernphys. Onderz., Amsterdam, Netherlands). *Chem. Weekbl.*, 1960, **56** (7), 94-98.—A review of recent developments in activation analysis is presented. Applications discussed include determinations of Pr in commercial ceric and lanthanum oxides and of Ce and Nd in samarium oxide.

M. J. MAURICE

See also Abstract—4151, Di-1-naphthylthiocarbazon as a reagent for Hg and Cu.

## 2.—INORGANIC ANALYSIS

General, determination of elements (arranged in the order of the Periodic Table), analysis of minerals and inorganic industrial products.

**4107. Limits of application of the polarographic method in inorganic analysis.** F. von Sturm (Forsch. Lab. Siemens-Schuckertwerke A.-G., Erlangen, Germany). *Z. anal. Chem.*, 1960, **173** (1), 11-17 (in German).—The lower limits of determination and of sensitivity for a square-wave polarograph have been measured for Zn, Pb, Cd, In, Tl and Mn. The determination of Pb in the presence of other elements is studied and the maximum tolerable ratios of 13 elements to Pb are reported.

T. R. ANDREW

4108. Separation of some heavy metals by solvent extraction and by paper chromatography. G. Weidmann (Kanonenweg 33, Coburg, W. Germany). *Canad. J. Chem.*, 1960, **38** (3), 459-464.—The partition coeff. of  $\text{FeCl}_3$ ,  $\text{CoCl}_2$  and  $\text{CuCl}_2$  between pure tri-*n*-butyl phosphate (I) and aq. HCl are reported;  $\text{NiCl}_2$  is not extracted by I. By using I,  $\text{Fe}^{3+}$  are easily separated from Ni, Co and  $\text{Cu}^{2+}$  at  $\approx 2 M$  HCl, then  $\text{Cu}^{2+}$  can be separated from Ni at  $\approx 8 M$  HCl, followed by Co from Ni at  $\approx 10 M$  HCl. A mixture of  $\text{Mn}^{2+}$ ,  $\text{Fe}^{3+}$ , Co, Ni and  $\text{Cu}^{2+}$  (as chlorides,  $\approx 10 \mu\text{g}$  of each per ml) can be separated (in  $\approx 4$  hr. at  $22^\circ$ ) by ascending paper chromatography with HCl-adjusted I (mixed with half its vol. of methanol) as solvent, the  $R_F$  values ensuring sharp separation. (Cf. Weidmann, *Anal. Abstr.*, 1960, 7, 152.) W. J. BAKER

4109. Studies on isobutyl methyl ketone extraction and the determination of metal salts. III. Metal oxinate complexes. Hidehiro Gotō and Yachiyo Kakita (Inst. for Iron, Steel and Other Metals, Tōhoku Univ., Katahira-cho, Sendai). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1959, **80** (12), 1448-1453.—The extraction of Zn, Mg and Be oxinates with isobutyl methyl ketone (I) (5 ml) is quant. from ammoniacal soln. (10 to 15 ml) of pH 9.4 to 11, 10.2 to 11, and  $\approx 9.2$  (in the presence of tartrate), respectively. A significant amount of the reagent is also extracted and absorbs at  $< 400 m\mu$ ; nevertheless, the extinction vs. concn. diagram is linear for Zn ( $< 60 \mu\text{g}$  per 5 ml), Mg ( $< 40 \mu\text{g}$ ) and Be ( $< 50 \mu\text{g}$ ) at 395, 385 and  $400 m\mu$ , respectively. The oxinates fluoresce (max. 545, 525 and  $530 m\mu$  for Zn, Mg and Be, respectively) in I, but the fluorescence fades rapidly on irradiation with u.v. light and is not suitable for analytical application. K. SAITO

4110. Spectrographic method for the analysis of high-purity acids. J. H. Oldfield and E. P. Bridge (Admiralty Materials Lab., Holton Heath, Poole, Dorset, England). *Analyst*, 1960, **85**, 97-104.—The impurities in the acids are concentrated as sulphates by evaporation with 0.1 N  $\text{H}_2\text{SO}_4$ . Copper sulphate is added as an internal standard, and the mixture is dried on a graphite electrode and excited by a d.c. arc in an atmosphere of argon and oxygen. The sensitivity for most of the 17 elements investigated is  $\approx 0.02 \mu\text{g}$ . Results obtained on samples of HCl,  $\text{HNO}_3$ , HF and acetic acid are quoted and discussed. A. O. JONES

4111. Chromatographic study of anionic complexes. IV. Separation of some ions in the presence of tartrate, with ethanol as solvent. E. J. Singh and Arun K. Dey (Chem. Lab., Univ. of Allahabad, India). *J. Chromatography*, 1960, **3** (2), 146-149 (in English).—The separation of  $\text{Cu}^{II}$ ,  $\text{Ni}^{II}$ ,  $\text{Co}^{II}$  and  $\text{Cd}^{II}$  in binary, ternary and quaternary mixtures of their tartrates is sometimes possible with ascending strip chromatography and 50 to 60% ethanol as solvent. Dimethylglyoxime,  $\text{H}_2\text{S}$ -water and  $\text{K}_4\text{Fe}(\text{CN})_6$  soln. alone or in mixtures are used as colour reagents. Tartrate is added to the metal soln. ( $\approx 0.05 M$ ); all binary mixtures except Co-Ni can be separated with a metal to tartrate ratio of  $\geq 0.9:1$ . With 3 or 4 components some separation is usually possible (except for Ni-Co-Cd) with a tartrate to metal ratio of  $\approx 0.6:1$ . P. D. PARR-RICHARD

4112. Metal nitrates in paper chromatography. VI. Systems containing tri-*n*-butyl phosphate and nitric acid. A. S. Kertes and A. Beck (Dept. of

Inorg. and Anal. Chem., Hebrew Univ. of Jerusalem, Israel). *J. Chromatography*, 1960, **3** (1), 195-196 (in English).—The use of tri-*n*-butyl phosphate (I) as an eluent in paper chromatography is discussed. In addition to ions known to be extracted from  $\text{HNO}_3$  by I, the following moved on the paper with appreciable  $R_F$  values—Ca, Mg, Al, Be, In, Mn, Se, Re, Fe, Mo, V, Tc, Bi, Zn and I. Covalent chlorides of Sb, Sn and Pd were also appreciably extracted by I. The concn. of nitrates or  $\text{HNO}_3$ , and of I in kerosene did not greatly affect the  $R_F$  values. P. D. PARR-RICHARD

4113. The use of Omega Chrome fast blue 2G in the micro-determination of some metals. A. A. A. El Raheem, A. A. Amin and A. S. Moustafa (Nat. Res. Centre, Cairo, Egypt). *Z. anal. Chem.*, 1960, **172** (5), 347-356 (in English).—The micro-determination of Mg, Ca and Mn is possible with EDTA by the use of Omega Chrome fast blue 2G (C.I. Mordant Blue 44) (I) as indicator; when present, Cd, Ni and Al are masked by the addition of CN- or triethanolamine. I is also used for the colorimetric determination of these cations; the accuracy for 4 to  $20 \mu\text{g}$  of Ca, 2 to  $5 \mu\text{g}$  of Mg, and 3 to  $10 \mu\text{g}$  of Mn is then within  $\pm 0.5$ , 5, and 3%, respectively. Aluminium can be determined by back-titration of excess of EDTA with a soln. of  $\text{Mg}^{2+}$  or  $\text{Ca}^{2+}$ , with I as indicator. I also forms a wine-red complex with Th, which is unaffected by EDTA or CN- and is suitable for the detection and colorimetric determination of Th (16 to  $40 \mu\text{g}$ ) in the presence of many cations; the accuracy is within  $\pm 1\%$ . J. P. STERN

4114. Titration of weak acids with an aluminium electrode. E. Scarano and S. Signoretti (Inst. Anal. Chem., Univ. Rome, Italy). *J. Electroanal. Chem.*, 1960, **1** (3), 218-225 (in English).—Aluminium is used as an indicator electrode (cf. *Anal. Abstr.*, 1957, **4**, 3814) in strongly alkaline soln. (pH  $> 9$ ) for the determination of NaOH in  $\text{Na}_2\text{CO}_3$  soln. by titration with HCl and for the determination of  $\text{NaHCO}_3$  in  $\text{Na}_2\text{CO}_3$  soln. by titration with NaOH. To obtain reproducible results, pre-treat the surface of the aluminium, which must be  $> 99.99\%$  pure, by smoothing with a file, immersion in 20% NaOH soln., anodic dissolution by electrolysis in  $N$  NaOH, removal of the oxide film by soaking in 20% NaOH soln. for 2 min., washing in  $N$  NaOH and immersion in  $N$  HCl for 1 min.; use the electrode immediately. De-oxygenate and stir the soln. by passing a rapid stream of hydrogen gas before and during the titration. A. R. ROGERS

4115. Separation of some fission isotopes by focusing ion-exchange. V. P. Shvedov, Ten Ten and A. V. Stepanov (Lensovet Inst. of Technol., Leningrad). *Zhur. Anal. Khim.*, 1960, **15** (1), 16-19.—Isotopes are separated on a paper bridge. The central part is immersed in  $\text{CCl}_4$ , one end in an anode soln. of HCl and the other in a cathode soln. of either citric acid or EDTA. The separation takes 5 min. with a current of 2 to  $10 \text{ mA}$  at 260 to 280 V. The mixtures  $^{90}\text{Sr}$ - $^{90}\text{Y}$ ,  $^{90}\text{Sr}$ - $^{90}\text{Y}$ - $^{144}\text{Ce}$ ,  $^{144}\text{Ce}$ - $^{140}\text{La}$  and Ce-Pr can be separated. Separation is incomplete with Ce-Pr mixtures at concn. up to  $0.5 \text{ mg}$  per ml. A. BURWOOD-SMITH

4116. New apparatus for the determination of water by the distillation method. L. Hübschen (Betriebslabor. der Wilh. Quester Maschinenfabrik, Köln). *Z. Lebensmittelforsch.*, 1960, **111** (5), 371-373.—In the apparatus described, the mixed vapours of water and immiscible solvent enter the

condenser at its top end, and in condensing wash down the water completely from the sides of the tube into the measuring capillary. Complete recoveries of known amounts of water up to 4 ml were obtained after 20 min. The apparatus is particularly suitable for tobacco, 20 g with 300 ml of xylene being distilled for 60 min.

C. L. HINTON

**4117. Chromatographic separation of some alkali metals.** E. C. Martin (Appl. Chem. School, Univ. of N.S.W., Sydney, Australia). *Anal. Chim. Acta*, 1960, **22** (2), 142-144.—A rapid and positive method of separation and identification is described. The solvent employed is methanol containing 5% of 15 N aq.  $\text{NH}_3$ , and bromophenol blue is used to identify the spots.

E. G. CUMMINS

**4118. Potassium phosphate as a reagent for the gravimetric estimation of lithium.** C. C. Patel and K. N. Vishweshwaraiah (Indian Inst. Sci., Bangalore 12, India). *Anal. Chem.*, 1960, **32** (2), 202-204.—The previous procedure (cf. Vishweshwaraiah and Patel, *Anal. Abstr.*, 1960, **7**, 872) has been modified by using potassium phosphate instead of 2-diethylaminoethanol-phosphate reagent. The potassium phosphate reagent is made by adding  $\text{H}_3\text{PO}_4$  to 8% aq. KOH soln. to pH 9.5. An aq. soln. of LiCl (10.0 ml, containing 5 to 50 mg of Li) is treated with phosphate reagent (6 ml) and water (4 ml) and kept at 65° to 70°; 1 hr. after pptn. 30 ml of abs. ethanol is added and heating is continued for 2 hr. The ppt. is collected while hot, ignited and weighed. The lithium factor is 0.1798. A correction of 0.36 mg is added for the solubility for each 50 ml of pptg. medium. Interference is caused by K and Na at levels much above three times that of the Li. Alkaline-earth and other metal salts interfere by co-precipitation. The reproducibility between duplicates is 0.3%.

R. M. S. HALL

**4119. Use of the glass electrode with a sodium function for determining the concentration of sodium ions.** V. E. Goremýkin and P. A. Kryukov. *Gidrokhim. Materialy*, 1959, **28**, 170-179; *Ref. Zhur.*, *Khim.*, 1959, (24), Abstr. No. 86,069.—It is shown that cells with a sodium glass electrode can be used to determine  $\text{Na}^+$  with a satisfactory accuracy if the diffusion potential is eliminated by means of a bridge of saturated KCl soln.. The activity coefficient  $\gamma_{\text{Na}}$  at ionic strength  $\mu \geq 0.05$  does not depend on the composition of the soln. but only on  $\mu$ . With  $\mu > 0.05$ ,  $\gamma_{\text{Na}}$  depends on  $\mu$  and on the anionic composition of the soln. If the anionic composition of the soln. is expressed as monovalent anions,  $\gamma_{\text{Na}}$  depends only on  $\mu$  and is independent of the cationic composition of the soln. even at  $\mu = 0.1$ . Equations are given for calculating  $\gamma_{\text{Na}}$  in soln. of  $\mu \geq 0.1$  of any composition.

C. D. KOPKIN

**4120. Determination of sodium ions in acidic silica sol systems. Solution potential measurement procedure.** T. A. Taulli (Inorganic Chemicals Div., Monsanto Chemical Co., St. Louis, Mo.). *Anal. Chem.*, 1960, **32** (2), 186-189.—An acidic silica sol is passed through the basic form of an anion-exchange resin (Dowex 1) and the pH value of the percolate is adjusted to  $6.0 \pm 0.2$ . When the  $\text{Na}^+$  concn. is  $< 100$  p.p.m., there is a linear relationship between the response of an indicating cationic electrode and log  $\text{Na}^+$  concn. A 0 to 280-mV potentiometer was used. The average

deviation between this method and conventional methods is 2 p.p.m. for values less than 100 p.p.m. For values between 200 and 400 p.p.m. the deviation is 20 p.p.m. Interference is caused by  $\text{Ca}^{2+}$  and  $\text{Fe}^{3+}$  at levels greater than twice the Na content. Lithium at above an equal level and  $\text{NH}_4^+$  and  $\text{K}^+$  interfere seriously.

R. M. S. HALL

**4121. Purification of sodium from oxides and control of its oxide content.** P. L. Kirillov, F. A. Kozlov, V. I. Subbotin and N. M. Turchin. *Atomnaya Energiya*, 1960, **8** (1), 30-36.—An apparatus is described for the determination of oxide concn. in liquid sodium used in heat exchangers. A "plug indicator" method is used, based on the fact that when the temp. of the sodium flowing through a small orifice falls below the oxide saturation temp., oxides are pptd. and block the orifice, thus reducing the flow. When the oxide pptn. temp. is known, the oxide concn. can be calculated from the equation  $W = 2.7 \times 10^{-4}(t/100)^{3.4}$ , where  $W$  is the solubility of O in Na (% by wt.) and  $t$  is the temp. The effects of rate of flow, orifice diameter and other variables are discussed. The method does not require precision instruments, and is accurate over a wide range of oxide concn. Cold traps of capacity 32 and 47 litres are described in which the concn. of O can be reduced to 0.002% by wt.

A. BURWOOD-SMITH

**4122. Micro-determination of potassium, rubidium and caesium with sodium tetraphenylboron by indirect potentiometric titration.** J. Havr (Military Acad., Brno, Czechoslovakia). *Coll. Czech. Chem. Commun.*, 1960, **25** (2), 595-597 (in German).—*Procedure*—Adjust the soln. of the sample (1 to 3 ml, containing  $< 40$   $\mu\text{g}$  of K, Rb or Cs) to pH 4 to 5 with acetic acid. Heat to  $\approx 60^\circ$  and add dropwise Na tetraphenylboron soln. (2%) (0.5 ml). Cool, filter off the ppt. on a glass filter (S3), wash with 2 drops of  $\text{H}_2\text{O}$  and then with a satd. soln. of K, Rb or Cs tetraphenylboron ( $3 \times 0.5$  to 1 ml). Transfer the filter to the pptn. beaker, dissolve the ppt. in acetone ( $3 \times 0.5$  ml), dilute the soln. with an equal vol. of  $\text{H}_2\text{O}$  and titrate potentiometrically with 0.01 N or 0.001 N  $\text{AgNO}_3$ .

J. ZFKA

**4123. Some factors affecting flame-photometric emission of rubidium in an oxygen-acetylene flame.** T. E. Shellenberger, R. E. Pyke, D. B. Parrish and W. G. Schrenk (Kansas Agric. Exp. Sta., Manhattan, U.S.A.). *Anal. Chem.*, 1960, **32** (2), 210-213.—The effect of relatively large quantities of  $\text{K}^+$  and other cations on the flame-photometric emission of Rb in an oxy-acetylene burner has been studied. When K is present in considerable excess the Rb line at 780  $\text{m}\mu$  is enhanced by overlapping of the K emission at 770  $\text{m}\mu$ . Sodium also causes enhancement, but Ca does not have any effect. When Mg is present at concn.  $> 60$  times that of Rb it has a depressing effect. Lithium is satisfactory for use as an internal standard, and the effect of K can be corrected by the use of a background-correction procedure with a chart recorder.

K. A. PROCTOR

**4124. Colorimetric determination of copper by means of  $\text{NN}'\text{N}''\text{N}'''$ -tetraphenylloxamidine.** M. Papafil, D. Furnica and N. Hurdur (Univ. "Al. I. Cuza," Iasi). *An. Ştiin. Univ. "Al. I. Cuza," Iasi*, 1959, **5** (1), 135-140.—The brown-red colour of the Cu complex with  $\text{NN}'\text{N}''\text{N}'''$ -tetraphenylloxamidine (I) in concn. of 0.42 to 43  $\mu\text{g}$  of Cu per ml is measured. *Procedure*—To the aq. copper



soln. is added 7 ml of an ethanolic 0.005 *M* soln. of **I**, followed by water and ethanol, so that the final soln. contains 65% of ethanol. The reading should be taken after 10 min.; the colour then remains stable for 2 hr. A large photocolormeter, model 4, is used, with a green filter. Nickel, Zn, Co, Mn, Cd and Cr do not interfere, even in concn. higher than that of the Cu. Aluminium interferes at concn. above twice that of Cu, while Fe produces large errors if its concn. is higher than that of Cu.

H. SHER

4125. Colorimetric determination of copper by means of bis(cyclohexanoneoxalylidihydrazone and oxalylidihydrazide). I. R. Capelle. *Chim. Anal.*, 1960, 42 (2), 69-77.—Bis(cyclohexanoneoxalylidihydrazone (**I**)) is an almost specific reagent for Cu, only Fe, Ni, Co and Cr interfering when present in a large excess. It is used for the determination of Cu in steel and cast iron free from Co, when the Ni content is < 20% and the Cu content < 0.5%. *Procedure*—The sample (0.5 g) is dissolved in 5 ml of HCl, 5 ml of HNO<sub>3</sub> and 10 ml of HClO<sub>4</sub> (d 1.61). The soln. is evaporated to fumes of HClO<sub>4</sub> and kept thus for  $\approx$  3 min. When cool, the soln. is diluted with  $\approx$  50 ml of H<sub>2</sub>O, filtered, and diluted to 250 ml. A 50-ml aliquot is treated with 2.5 ml of citric acid soln. (200 g per litre), 11 ml of aq. NH<sub>3</sub> (1:9) and 2 ml of reagent [0.5 g of **I** in 100 ml of aq. ethanol (1:1)]. The soln. is diluted to 100 ml and its extinction is measured after 30 min. against a reagent blank at  $\approx$  600 m $\mu$ . Calibration is achieved by addition of varied amounts of standard copper soln. (1 ml = 0.010 mg) to the reagents. Oxalylidihydrazide gives a more intense colour than **I** with Cu, and is less sensitive to variations in pH.

II. R. Capelle. *Ibid.*, 1960, 42 (3), 127-135.—Oxalylidihydrazide in the presence of acetaldehyde is superior to **I** for the colorimetric determination of Cu. An intense violet colour is given with Cu<sup>2+</sup>, which is stable over a fairly wide pH range, with a max. stability at pH 8.7 to 8.8. The extinction of the complex is read at 540 m $\mu$ . Few ions interfere. The reagent is suitable for the determination of Cu in steel and a variety of alloys and metals.

III. R. Capelle. *Ibid.*, 1960, 42 (4), 181-190.—Full details are given for the colorimetric determination (with oxalylidihydrazide in the presence of acetaldehyde) of Cu in steel and cast iron (0 to 1% of Cu), aluminium and magnesium and their alloys (0 to 0.5%), zinc, lead and tin (0 to 0.1%), nickel (0 to 0.2%), zirconium (0 to 0.0025%), titanium (0 to 0.00125%) and uranium and its salts (0 to 0.5%).

J. H. WATON

4126. Use of *p*-anisidine in chemical analysis. Study of the reaction of copper ions with *p*-anisidine and the colorimetric determination of copper in nickel and zinc alloys and coloured glass. V. N. Podchalnova and G. G. Loseva. *Izv. Vyssh. Uchebn. Zavedenii. Khim. i Khim. Tekhnol.*, 1959, 2 (3), 316-321; *Ref. Zhur.*, 1959, (24), Abstr. No. 86,078.—The reaction of Cu<sup>2+</sup> with *p*-anisidine and KSCN is studied; the optimum conditions for the formation of the *p*-anisidine-thiocyanate complex of Cu are—*p*-anisidine concn.  $7 \times 10^{-3}$  to  $3 \times 10^{-3}$  *M*, KSCN concn. 0.02 to 2.0 *M*, pH 4.0 to 5.5. Beer's law is obeyed for copper concn. of from  $5 \times 10^{-4}$  to  $3 \times 10^{-4}$  *M*; the sensitivity of the reaction is  $6.0 \times 10^{-7}$   $\mu$ g per ml. A photometric method is developed for determining Cu in zinc and nickel alloys and in coloured glass.

C. D. KOPKIN

## 4127. Use of quinol and similar reducing agents.

XIV. Reductometric determination of copper with quinol. M. Pavliková and J. Zýka (Inst. Anal. Chem., Charles' Univ., Prague). *Z. anal. Chem.*, 1960, 172 (5), 321-325 (in German).—Since Cu<sup>II</sup> is quant. reduced by quinol to Cu<sup>I</sup> it can be determined potentiometrically in the presence of SCN<sup>-</sup>, which precipitate CuSCN. No interference is given by Ag, Hg<sup>I</sup>, Ni, Ba, Zn, Mn<sup>II</sup>, Ca, Co<sup>II</sup>, Pb, Cd, Al, As or Sb, or by Cl<sup>-</sup> or SO<sub>4</sub><sup>2-</sup>. Positive errors are caused by NO<sub>3</sub><sup>-</sup> (1%) and by PO<sub>4</sub><sup>3-</sup>, Br<sup>-</sup> and BrO<sub>3</sub><sup>-</sup>; and NO<sub>2</sub><sup>-</sup>, I<sup>-</sup>, S<sup>2-</sup>, S<sub>2</sub>O<sub>3</sub><sup>2-</sup>, SO<sub>3</sub><sup>2-</sup>, [Fe(CN)<sub>6</sub>]<sup>4-</sup> and [Fe(CN)<sub>6</sub>]<sup>3-</sup> interfere. The method is rapid, accurate to within  $\pm$  0.3% on 20 mg of Cu, and of use, for example, in the analysis of aluminium bronze. *Procedure*—Add 10% Na acetate soln. (25 ml), NH<sub>4</sub>Cl (3 g) and 10% NH<sub>4</sub>SCN soln. (5 to 10 ml) in this order to the sample containing 8 to 25 mg of Cu<sup>2+</sup>. Dilute to 75 ml and titrate potentiometrically with 0.1 to 0.025 *N* quinol; the potential change at the end-point is 2500 mV per ml. The redox potential is about 240 mV. J. P. STERN

## 4128. Spectrophotometric determination of copper with ammonium pyrophosphate.

C. J. Keatch (Inorg. Res. Lab., Chem. Dept., Battersea College of Technol., London, England). *Talanta*, 1960, 3 (4), 351-355 (in English).—The Cu<sup>II</sup>-ammonium pyrophosphate complex obtained from copper soln. (adjusted to a pH of < 10 with dil. aq. NH<sub>3</sub>) and 0.2 *M* ammonium pyrophosphate is used for the determination of Cu in the range 7 to 30 mg per ml, and is suitable for the analysis of alloys when Cu is a major constituent. The extinction is measured at 650 m $\mu$ , and Beer's law is obeyed up to 1.2 mg of Cu per ml. There is no interference from Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, ClO<sub>4</sub><sup>-</sup>, Sn<sup>II</sup>, Zn, Cd or Mn; when the test soln. is made ammoniacal before the addition of the reagent, Pb and Bi are pptd. and can be separated. Cobalt and nickel interfere and appropriate corrections must be made. The standard deviation (5 determinations) on an average extinction at 650 m $\mu$  of 0.278 is  $\pm$  0.002. R. M. S. HALL

4129. Rapid method for the determination of copper in metallic silver and silver nitrate. W. Kemula, K. Brajter, S. Cieřlik and H. Lipińska (Dept. of Inorg. Chem., Univ., Warsaw). *Chem. Anal.*, Warsaw, 1959, 4 (5-6), 855-861.—Silver is separated from Cu on the cation exchanger Wofatit KPS-200. The Ag is pptd. on the column by HCl, and the Cu is eluted as the complex CuCl<sub>4</sub><sup>2-</sup> and determined polarographically or colorimetrically. This method can be used to determine 0.002 to 0.1% of Cu in metallic silver or silver nitrate. The precision is  $\pm$  5.0%. L. SMAKOWSKI

## 4130. Analysis by activation. III. Simultaneous determination of copper and uranium in minerals by radioactivation.

A. Abrao (Univ. São Paulo, Brazil). *Inst. Energia Atomica, São Paulo, Rep. IEA/RQ-8*, Apr., 1959. 15 pp.—Copper and U are frequently associated in the same mineral and can be qual. and quant. determined by means of the radio-isotopes <sup>106</sup>Au and <sup>232</sup>Np formed during the irradiation of the mineral in a reactor. The Cu is separated from the neptunium and fission products by the use of an anion-exchange resin without the addition of isotopic carriers. The efficiency of the chemical separation and the purity of the two radio-isotopes is controlled by  $\gamma$ -spectroscopy and by determination of the two half-lives.

NUCL. SCI. ABSTR.

## 4131. Decomposition of ferrocyanide in analysis.

**I. New spot test for silver.** I. Kraljić (Inst. Anal. Chem., Fac. of Technol., Zagreb Univ., Yugoslavia). *Croat. Chem. Acta*, 1960, **32** (1), 43-47 (in English).—The test is based on the catalytic action of  $\text{Ag}^+$  on the decomposition of  $[\text{Fe}(\text{CN})_6]^{4-}$  in the presence of nitrosobenzene (**1**) to give an intensely violet-coloured product. **Procedure**—Place, in succession, one drop of aq.  $\text{K}_4\text{Fe}(\text{CN})_6$  soln. (0.25 or 0.5%), one drop of a mixture of a satd. aq. soln. of **1** and acetate buffer (pH 3.5) (4:1), and one drop of the sample soln. on a porcelain plate or in a micro test-tube, and warm the mixture to  $\approx 60^\circ$ , adding further drops of buffered **1** soln. if necessary. A deep pink colour developing after several min. indicates the presence of Ag. A blank should be run concurrently. The lower limit of detection is  $0.004 \mu\text{g}$  per 0.035 ml. Gold and Hg also react positively:  $\text{Fe}^{3+}$ ,  $\text{As}^{3+}$ ,  $\text{Mn}$ ,  $\text{Pb}$ ,  $\text{I}^-$ ,  $\text{SO}_3^{2-}$  and  $\text{S}_2\text{O}_3^{2-}$  seriously decrease the sensitivity. Any coloured ferrocyanide ppt. formed by, e.g.,  $\text{Cu}^{2+}$  or  $\text{UO}_2^{2+}$ , should be destroyed by addition of aq.  $\text{NH}_3$  or  $\text{NaOH}$ . The test should be carried out in diffused or artificial light. W. J. BAKER

**4132. Photometric determination of silver by means of copper thiuramate and thiuram [disulphiram].** A. L. Gershuns and L. Z. Kalm'kov (Sci. Res. Inst. of Chem., A. M. Gorki Kharkov State Univ.). *Zavod. Lab.*, 1960, **26** (2), 152-153.—Disulphiram forms with Cu a brown complex insol. in water and easily sol. in benzene. The max. absorption of the soln. is at  $435 \text{ m}\mu$ . The soln. is not affected by shaking it with aq. soln. over a wide pH range, and it is decolorised only by salts of mercury and silver. The complex is stable indefinitely in the solid state. Disulphiram is suitable as a reagent for determining Cu in various alloys, the pH of the soln. being almost immaterial, but Co, large amounts of Ni, and free  $\text{HNO}_3$  interfere. To prepare the Cu complex for the purpose of determining Ag in various materials 150-ml amounts of saturated soln. of disulphiram and  $\text{CuSO}_4$  in ethanol-water (1:1) are mixed, and the ppt. is collected, washed with water and ethanol, and dried. The complex is then dissolved in benzene to give a soln. with an extinction of  $\approx 1$ . A sample soln. containing Ag (10 to  $150 \mu\text{g}$  per ml) is diluted to 15 ml and mixed with 10 ml of the reagent soln. The extinction of the benzene soln. is determined. Mercury and  $\text{HNO}_3$  interfere. G. S. SMITH

**4133. Amperometric titration of silver and mercury with thiourea solution.** Yu. I. Usatenko and A. I. Shumskaya (F. E. Dzerzhinskii Dniepropetrovsk Chem. Tech. Inst.). *Zavod. Lab.*, 1960, **26** (2), 149-152.—In 0.5 to 6 N  $\text{HNO}_3$  Ag can be titrated amperometrically on a rotating platinum electrode at +1.0 V with 0.02 M thiourea. In  $\text{HNO}_3$  or  $\text{H}_2\text{SO}_4$  soln. over the whole range from 0.01 N to dilutions of 1:1, but not in HCl soln. of concn.  $> 0.001 \text{ N}$ , Hg can be titrated similarly. **Procedure for Ag in copper-silver alloys**—The sample (0.6 to 0.7 g) is dissolved in a small amount of dil.  $\text{HNO}_3$  (1:1), oxides of N are removed, and the soln. is diluted to 1 litre. An aliquot (10 ml) is diluted to 50 ml with N  $\text{HNO}_3$  and titrated with thiourea soln. **Procedure for Hg in mercury ores**—The sample (0.5 to 1 g) is moistened with water and stirred with 5 ml of conc.  $\text{H}_2\text{SO}_4$ , then treated with  $\approx 0.5 \text{ g}$  of solid  $\text{KMnO}_4$  in small portions, and stirred with a further 5 ml of conc.  $\text{H}_2\text{SO}_4$ . After 30 min. the mixture is heated gradually to boiling. After addition of 5 ml of water, 3%  $\text{H}_2\text{O}_2$  soln. is

added dropwise until the  $\text{KMnO}_4$  is decomposed, the soln. is then evaporated to fuming, the cooled soln. is diluted to 50 ml and the Hg is titrated.

G. S. SMITH

**4134. The micro-determination of gold with p-dimethylaminobenzylidenerhodanine.** T. M. Cotton and A. A. Woolf (A.E.I. Ltd., Aldermaston, Berks., England). *Anal. Chim. Acta*, 1960, **22** (2), 192-194.—Details of the extraction of the coloured gold complex into isoamyl acetate are given. Deviations within  $\pm 2\%$  are reported for determinations in the range 4 to  $14 \mu\text{g}$  of Au, measured at  $515 \text{ m}\mu$ . E. G. CUMMINS

**4135. Detection of beryllium and emission-spectrographic detection of mercury vapour in air.** D. Fromm and A. von Oer (I Phys. Inst., Univ. München). *Mikrochim. Acta*, 1960, (2), 235-244 (in German).—For the spectrographic detection of traces of Be in soln. or in organic materials, carbon, copper or silver electrodes may be used, with the line Be I 2348 Å for the arc method, and the doublet Be II 3131.32 - 3131.97 Å for the spark method. The drop size is 0.007 ml, and as little as  $7 \times 10^{-4} \mu\text{g}$  of Be can be detected. For Be in airborne particles the contaminated air is led through the hollowed electrodes enclosed in a glass bulb;  $\approx 9 \times 10^{-2} \mu\text{g}$  of Be per cubic metre is detectable. The detection of Hg in air was studied by passing air containing known amounts of Hg vapour through the enclosed electrodes as described above. The line used was Hg 4358.34 Å, and the density of the recorded line was equiv. to about 5% of the total Hg passed through the apparatus. About  $4 \mu\text{g}$  of Hg per litre of air could be detected. H. M.

**4136. Determination of small amounts of beryllium by means of  $\beta$ -diketones.** E. S. Przheval'skii and L. M. Moiseeva (M. V. Lomonosov Moscow State Univ.). *Zhur. Anal. Khim.*, 1960, **15** (1), 117-118.—Two gravimetric methods are described for the determination of Be by its pptn. with either 2:2-dimethylhexane-3:5-dione or 3-propylpentane-2:4-dione. The advantages of these methods are the low conversion factor of 0.03096 in each case and the non-hygroscopic nature of the residue.

A. BURWOOD-SMITH

**4137. Apparatus for the routine determination of the oxygen content of beryllium metal by activation.** R. F. Coleman and J. L. Perkin (U.K.A.E.A., Atomic Weapons Res. Estab., Aldermaston, Berks., England). *Analyst*, 1960, **85**, 154-155.—The automatic operation described replaces the manual transfer of the sample to the counter after irradiation as was the practice reported previously (*Ibid.*, 1959, **84**, 233). The sample is placed in a polystyrene holder, 6 in. long, that allows the sample to move from the end subjected to irradiation to the other end during its passage along a 15-ft. tube to the shielded counter. The part of the holder near the counter thus has little activity, as it has been some distance from the neutron source. The counting system for determining the  $^{10}\text{B}$  activity is described.

A. O. JONES

**4138. Separation of magnesium from sodium and potassium. A tracer study.** A. H. A. Heyn and H. L. Finston (Dept. of Chem., Univ., Boston, Mass., U.S.A.). *Anal. Chem.*, 1960, **32** (3), 328-332.—The separation from Na and K of Mg as  $\text{MgNH}_4\text{PO}_4$ , or as Mg oxalate by pptn. from



homogeneous soln. or as Mg 8-hydroxyquinolate, both by the usual method and by pptn. from homogeneous soln. with urea, is followed radiometrically. The amount of Na and K co-pptd. is negligible in all cases except in the phosphate method (single pptn.); K interferes less than Na. It is suggested that the alkali metal may replace some of the Mg by a process of "anomalous isomorphous substitution." The least interference is shown in the 8-hydroxyquinoline methods; pptn. from homogeneous soln. results in only one-third of the Na being co-pptd. as compared with the conventional method.

J. H. WATON

**4139. Spectrographic determination of magnesium with a "pumping" electrode.** Saburo Yanagisawa and Yoshikazu Hashimoto (Fac. of Engng, Keio Univ., Koganei, Tokyo). *Japan Analyst.*, 1959, **8** (9), 582-588.—A "pumping" graphite electrode was prepared by mounting graphite powder (120 to 200 mesh) in a hole (diameter 1.5 mm) bored in a graphite electrode (diameter 6 mm, length 25 mm). The sample soln., containing  $< 1 \mu\text{g}$  of Mg per ml, Zn (50 mg per ml) as internal standard and 2 N HCl, is placed in a shallow dish, in which the electrode is held upright. An intermittent arc (110 V, 1.5 amp.; interruption factor, 0.125; period, 1.5 sec.; preliminary discharge, 1 min.; exposure, 1 min.) is struck between this electrode and a graphite anode (diameter 1 mm) and the Mg line at 2795.5 Å is compared with Zn 2756.4 Å. The error is  $< 20\%$ . This method is used for the analysis of natural water.

K. SAITO

**4140. Rapid determination of calcium in calcium-silicon and ternary alloys of aluminium-calcium-silicon.** H. Drost. *Arch. Eisenhüttenw.*, 1959, **30** (10), 599-600.—The powdered sample (0.2 g) is mixed with charcoal powder and heated for 10 min. at  $550^\circ$  to  $600^\circ$  in a stream of dry Cl free from  $\text{CO}_2$  and O. After volatile chlorides have been expelled in a stream of N, the residue is extracted with  $\text{H}_2\text{O}$  and the chloride is determined with 0.1 N  $\text{AgNO}_3$  and  $\text{K}_2\text{CrO}_4$ . The Mg present in these alloys (0.1 to 0.15%) does not interfere, but high contents of Al introduce inaccuracies. The determination can be completed in 20 min.

J. H. WATON

**4141. Indirect colorimetry of strontium.** Toru Nozaki (Fac. of Engng, Ehime Univ., Niigama). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1959, **80** (11), 1278-1281.—Two methods were examined and optimum conditions are given. Strontium ( $< 0.5 \text{ mg}$ ) is treated with  $\text{K}_2\text{CrO}_4$  soln. (25%) (0.06 ml) and aq.  $\text{NH}_3$  soln. (sp. gr. 0.88) (0.08 ml), and filtered with a filter-stick. The ppt. is washed with ethanol (1:1, containing one-tenth of its vol. of conc. aq.  $\text{NH}_3$  soln.) (0.5 ml), then dissolved in 2 N HCl (0.5 ml), and the soln. is diluted to 10 ml. The Cr is determined colorimetrically as  $\text{Cr}_2\text{O}_7^{2-}$  (for  $> 100 \mu\text{g}$  of Sr), or with diphenylcarbazide soln. (0.2% in 50% acetone) (1 ml) and  $\text{H}_2\text{SO}_4$  (6 N) (0.8 ml). In the presence of  $\text{Ca}^{2+}$ , the working curve must be modified. Strontium chloride is also determined colorimetrically as  $\text{Cl}^-$  with  $\text{Hg}(\text{SCN})_2$  in ethanol (Iwasaki et al., *Bull. Chem. Soc. Japan*, 1952, **25**, 226) after being freed from other metal ions by the use of cation-exchange resin Dowex 50.

K. SAITO

**4142. Studies on solvent extraction by the use of radio-isotopes. V. Extraction of strontium-90 and yttrium-90 with 2-thenoyltrifluoroacetone in**

**benzene.** Nobuo Suzuki and Toyooki Kato (Chem. Dept., Fac. of Sci., Tôhoku Univ., Katahira-cho, Sendai). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1959, **80** (10), 1148-1151.—Whereas  $^{90}\text{Y}$  is extracted free from Sr with 0.1 M 2-thenoyltrifluoroacetone in benzene from an aq. soln. of pH 6 to 9 (Strode and Kinderman, *Phys. Rev.*, 1954, **93**, 1029)  $^{90}\text{Sr}$  is also extracted at pH 8 in the presence of dioxan. The rate of extraction increases with increase in amount of dioxan and becomes constant in the presence of 40% (by vol.) of dioxan. Both Sr and Y are back-extracted from the benzene soln. with dil. mineral acid.

K. SAITO

**4143. Determination of minute amounts of barium by flame photometry.** M. Dzubay (S. Hungarian Agric. Res. Inst., Szeged). *Acta Chim. Acad. Sci. Hung.*, 1960, **22** (1), 65-68.—This is an English version of a paper published, in Hungarian, in *Magyar Kém. Foly.*, 1958, **64**, 483; cf. *Anal. Abstr.*, 1959, **6**, 3418.

J. H. WATON

**4144. New back-titrimetric method for the determination of zinc with methyl red as adsorption indicator.** Takanosuke Nasu (Tôhoku Univ., Sendai, Japan). *Technol. Rep. Tôhoku Univ.*, 1959, **24** (1), 1-10 (in English).—The procedure given ensures a sharp end-point (pale-yellow to blue) and is applicable to soln. containing from 0.1 to 1 mg of Zn per ml. The sample soln. ( $\approx 10 \text{ ml}$ ) is adjusted to pH 1 to 1.8 and heated to  $60^\circ$  to  $70^\circ$  and a slight excess of 0.1 M potassium ferrocyanide (15 ml) is added, followed by ten drops of a 0.1% ethanolic soln. of methyl red as internal indicator. The excess of potassium ferrocyanide is then titrated potentiometrically with 0.15 M  $\text{ZnCl}_2$ . The presence of  $\text{Mg}^{2+}$  or  $\text{Sr}^{2+}$  obscures the end-point. [No data on the accuracy are given.]

W. J. BAKER

**4145. Chemical analysis with organic reagents. X. Volumetric determination of zinc with 2-hydroxy-1-naphthaldoxime.** Michio Mashima (Fac. of Engng, Niigata Univ., Nagaoka, Niigata-ken). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1959, **80** (11), 1270-1272.—2-Hydroxy-1-naphthaldoxime (I) (Endo et al., *Ibid.*, 1953, **74**, 565) forms a ppt. with Zn at pH  $> 4.6$ . The pptn. is quant. in ammoniacal soln. of pH  $> 9$ . The ppt. is filtered off, dissolved in a known amount of 0.1 N  $\text{H}_2\text{SO}_4$  ( $> 10 \text{ ml}$  per 10 mg of Zn) and the excess of acid in the filtrate is titrated with NaOH soln. Nickel and Cu are pptd. with I in an acetic acid soln. of pH  $< 4.6$ , and Zn is then pptd. at pH 9.

K. SAITO

**4146. Quantitative determination of zinc by precipitation chromatography.** I. N. Grigorenko, N. L. Olenovich and A. A. Morozov (I. I. Mechnikov Odessa State Univ.). *Zhur. Anal. Khim.*, 1960, **15** (1), 115-116.—A method for the determination of Zn in the presence of  $\text{Cr}^{3+}$  is described. The precipitating agent is  $\text{Na}_2\text{S}_2\text{O}_8 \cdot \text{H}_2\text{O}$ , used in a carrier of agar gel in the ratio 2:5, and the pptn. time is 24 hr. Details are given of the ZnS zone widths obtained in the determination of Zn in ternary mixtures of  $\text{Zn}^{2+}$  -  $\text{Cr}^{3+}$  -  $\text{Hg}^{2+}$  and  $\text{Zn}^{2+}$  -  $\text{Cr}^{3+}$  -  $\text{Ag}^+$ , and the variation of these zone sizes with  $\text{Zn}^{2+}$  concn. The determination can be carried out on small vol. of test soln. (e.g., 0.5 to 1.0 ml).

A. BURWOOD-SMITH

**4147. Photometric determination of small amounts of zinc in bearing metal.** N. V. Kostin (School of Anal. Chem., Moscow Univ.). *Vestn. Moskov.*

*Univ.*, 1960, (1), 49-53.—To determine  $< 0.005\%$  of Zn in Pb-Sn-Sb bearing metal, dissolve 0.05 to 0.1 g of the finely ground metal in a porcelain dish in 4 ml of conc. HCl and  $\text{HNO}_3$  (3:1) with warming. Evaporate the soln. on a sand bath to remove oxides of N, treat the residue with 10 ml of HCl, filter off the undissolved  $\text{PbCl}_2$ , and wash it with dil. HCl ( $\times 2$ ). Collect the filtrate and wash liquors in a 100-ml separating-funnel, add 6 or 8 drops of dil.  $\text{H}_2\text{SO}_4$  and 10 ml of 40%  $\text{NH}_4\text{SCN}$  soln. Extract the thiocyanate complexes of Zn, Cu, Cd and Ni with 15 ml of isoamyl alcohol, and wash the extract with  $\text{NH}_4\text{SCN}$  soln. acidified with  $\text{H}_2\text{SO}_4$  (200 ml of water, 50 ml of 40%  $\text{NH}_4\text{SCN}$  soln. and 20 drops of dil.  $\text{H}_2\text{SO}_4$ ) to re-extract Cu, Cd and Ni. Separate the washed extract and add 15 ml of ammoniacal  $\text{NH}_4\text{Cl}$  soln. (200 ml of water, 15 ml of 20%  $\text{NH}_4\text{Cl}$  soln. and 25 ml of 25% aq.  $\text{NH}_3$ ), shake, separate the aq. phase containing the ammonium zincate into a 100-ml separating-funnel, adjust the pH to 6 with a buffer soln. of equal volumes of N Na acetate and 4 N acetic acid (Na alizarinsulphonate indicator), and extract with 2-ml or 3-ml portions of 0.005% dithizone soln. in  $\text{CCl}_4$  until the colour of the dithizone soln. remains unchanged. Make the extracts up to 50 ml with  $\text{CCl}_4$  and measure the extinction of the soln. Construct a calibration curve from a standard sample of zinc. The preparation of the reagent soln. is described. In determining 0.0103 and 0.0014% of Zn, the abs. error was  $\pm 0.0001\%$  in each case. The method was also tested on synthetic mixtures containing salts of Sn, Cu, Sb, Pb, Cd, Co, Bi and Zn; with 6, 8, 10 and 12  $\mu\text{g}$  of Zn in samples of about 0.1 g, the amounts determined were 5.9, 7.8, 10.3 and 12.1  $\mu\text{g}$ , respectively.

C. D. KOPKIN

**4148. Polarographic determination of a small amount of zinc in cadmium with the aid of thiocyanate extraction.** Genkichi Nakagawa (Dept. of Ind. Chem., Nagoya Inst. Tech., Gokiso-cho, Showa-ku, Nagoya). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1959, **80** (10), 1145-1148.—The extraction of Zn with ethyl ether from N HCl soln. containing M KSCN is effected with a yield of  $\approx 95\%$ , but a significant amount of Cd is found in the ether layer, which is washed with N HCl containing M KSCN. The rate of extraction decreases with increase in ionic strength, to an extent that increases in the sequence  $\text{Cl}^-$ ,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$ . The ether layer is evaporated and mixed with M Na acetate (1 ml), gelatin soln. (0.1%) (5 ml) and water (to a total vol. of 100 ml) and the pH is adjusted to between 4.0 and 5.5 before recording the polarogram.

K. SAITO

**4149. Determination of small amounts of cadmium. I. Separation of cadmium from zinc with hydrogen sulphide.** V. P. Pazumova. *Trudy Leningr. Politekh. Inst.*, 1959, (201), 136-140; *Ref. Zhur., Khim.*, 1959, (24), Abstr. No. 86,090.—The possibility of quantitatively separating Cd from Zn by a single pptn. with  $\text{H}_2\text{S}$  from acid soln. is studied with the radioactive isotope  $^{109}\text{Cd}$ . Earlier data (Zollner, *Z. anal. Chem.*, 1938, **114**, 8) on the separation of Cd from small amounts of Zn (2 to 4 times the Cd content) by a single pptn. with  $\text{H}_2\text{S}$  from a hot soln. strongly acidified with  $\text{H}_2\text{SO}_4$  are confirmed. It is shown that the  $\text{CdS}$  ppt. obtained from nitric acid soln. is not chemically pure.

**II. Photometric determination of cadmium with cation.** V. P. Pazumova. *Ibid.*, 1959, (201), 141-149.—The optimum conditions for the analysis

are determined. For 25 ml of soln., containing 0.05 to 0.70  $\mu\text{g}$  of Cd per ml, it is necessary to use 0.75 ml of a 0.02% ethanolic soln. of cation in 0.02 N KOH, 2.0 ml of a 0.25% gelatin soln. and 7 ml of 2 N KOH. The optical densities are measured at 400 to 500  $\text{m}\mu$  30 to 40 min. after preparing the soln. Beer's law is obeyed for the concn. range of Cd of 0.05 to 0.70  $\mu\text{g}$  per ml. The sensitivity is 0.05  $\mu\text{g}$  of Cd per ml.

**III. Determination of cadmium with cation in the presence of other ions.** V. P. Pazumova. *Ibid.*, 1959, (201), 150-157.—It is shown that small amounts of Cd (0.10 to 0.70  $\mu\text{g}$  per ml) can be determined in the presence of 1500  $\mu\text{g}$  of Zn, 2000  $\mu\text{g}$  of Pb, 1500  $\mu\text{g}$  of Al and 3000  $\mu\text{g}$  of K per ml without preliminary separation. Interference due to  $\text{Fe}^{3+}$  is removed by adding Na K tartrate. The copper content should be  $> 10 \mu\text{g}$  per ml. The method is used to determine Cd in standard samples of metallic zinc and aluminium, the mean relative error being  $\pm 2\%$ .

C. D. KOPKIN

**4150. Titrations of mercury(II) with Variamine blue as redox indicator. Determination of cyanide and mercuric ions.** Z. Gregorowicz and F. Buhl (Silesian Tech. High School, Gliwice, Poland). *Z. anal. Chem.*, 1960, **173** (2), 115-121 (in German).—The method permits determination of  $\text{CN}^-$  by  $\text{Hg}^{2+}$  and conversely of  $\text{Hg}^{2+}$  by  $\text{CN}^-$ , and is based on the formation of undissociated  $\text{Hg}(\text{CN})_2$ . Procedure for the determination of  $\text{CN}^-$ —Add 0.1 N  $\text{Hg}_2(\text{NO}_3)_2$  (1 drop) and buffer soln. of pH 4.6 (10 ml) to the sample (5 to 50 mg of  $\text{CN}^-$ ); then add rapidly 0.1 N  $\text{Hg}(\text{NO}_3)_2$ , followed, just before the end-point, by 1% Variamine blue (C.I. Azoic Diazo Component 35) (2 drops) and titrate slowly with 0.1 N  $\text{Hg}(\text{NO}_3)_2$ . At the end-point the violet colour persists. Determination of  $\text{Hg}^{2+}$ —Add buffer (pH 4.6) (10 ml) to the sample containing  $\text{Hg}^{2+}$  (40 to 400 mg). Add a small excess of 0.1 N KCN, then 0.1 N  $\text{Hg}_2(\text{NO}_3)_2$  (1 drop) and indicator (2 drops) and titrate the excess of  $\text{CN}^-$  with 0.1 N  $\text{Hg}(\text{NO}_3)_2$ . The accuracy for 5 to 20 ml of 0.1 N KCN is  $\pm 1\%$  and for 4 to 16 ml of 0.1 N  $\text{Hg}(\text{NO}_3)_2$  is  $\pm 0.15\%$ .

J. P. STERN

**4151. Syntheses of derivatives of dithizone and their application to analytical chemistry. IV. Suitability of di-1-naphthylthiocarbazon for the determination of mercury and copper.** Shinsuke Takei and Takio Kato (Tōhoku Univ., Sendai, Japan). *Technol. Rep. Tōhoku Univ.*, 1959, **24** (1), 85-94 (in English).—In the determination of  $\text{Hg}^{2+}$  by extraction with  $10^{-4}$  to  $10^{-6}$  M di-1-naphthylthiocarbazon (**I**) at pH 3 to 5 and measurement of the extinction of the filtered organic phase at 525  $\text{m}\mu$ , 0.01 M EDTA must be added in excess to screen  $\text{Cu}^{2+}$  or  $\text{Bi}^{3+}$ , and thiocyanate to mask Ag. Unlike the extraction with  $o,o'$ -dimethyldithizone (**II**) (cf. Takei and Kato, *Anal. Abstr.*, 1958, **5**, 767, 2550), a max. of  $\approx 200$  mg each of Zn, Cd, Pb, Co and Ni can be tolerated without the need for screening. The sensitivity of **I** is greater than that of **II** and the extraction of  $\text{Hg}^{2+}$  is quant. in the presence of a large excess of  $\text{Cl}^-$ . For the determination of  $\text{Cu}^{2+}$  by quant. extraction with **I** at pH 2 to 4 (Na acetate-HClO<sub>4</sub> buffer) followed by measurement of the extinction of the filtered extract at 560  $\text{m}\mu$ , **I** is superior to dithizone in sensitivity and specificity of reaction, but is inferior to **II** in specificity although formation of the enol complex does not occur. A max. of  $\approx 25$  to 50 mg of Ni, Co, Zn and Cd can be tolerated but, unless removed by re-extraction into aq. KBr,  $> 3$  mg of Bi causes low

results. In amounts  $< \approx 3$  mg, Bi can be screened by adjusting the sample soln. to pH 2 and 0.2 M in NaBr before the extraction. W. J. BAKER

**4152. Colorimetric determination of boron in nitrate solutions.** W. J. Ross and J. C. White (Anal. Chem. Div., Oak Ridge Nat. Lab., Tennessee, U.S.A.). *Talanta*, 1960, **3** (4), 311-317 (in English).—Boron in concn.  $< 100$  p.p.m. in 0.5 to 3.0 M nitrate soln. can be determined with carminic acid if the nitrate is destroyed by heating the sample soln. under reflux with  $H_2SO_4$  and formic acid. To the cooled soln. are added HCl,  $H_2SO_4$  and carminic acid, and, after 45 min., the extinction is measured at 585 or 610  $m\mu$  against a reagent blank. The concn. of B is read from a calibration curve. The coeff. of variation is 1% (15 determinations) at the 25- $\mu g$  level rising to 5% (5 determinations) at 12.5  $\mu g$ ; this increased error is thought to be due to  $CO_2$  bubbles interfering with the optical measurements. Uranium interferes at U to B ratios of 1000, and must therefore be extracted with tri-n-octylphosphine oxide when the method is applied to nuclear fuels. R. M. S. HALL

**4153. Separation and determination of boron in silicate by sintering with zinc oxide and sodium carbonate.** Yoshiro Moriya (Gov. Ind. Res. Inst., Saidacho, Ikeda, Osaka). *Japan Analyst*, 1959, **8** (10), 667-671.—When a silicate containing 0.5 to 20% of B is sintered with a mixture of ZnO and  $Na_2CO_3$  at 900° for 10 min. and extracted with water, B is quant. dissolved as borate, whereas only a small amount of Si is found in the aq. phase. The amount of dissolved Si decreases with increase in amount of B (e.g.,  $\approx 10$  mg of  $SiO_2$  for 1%, and  $\approx 1$  mg for 20% of B) and its interference with the alkalimetric titration of B is corrected by means of an empirical table. Metal ions are removed with the cation-exchange resin Amberlite IR-120 ( $Na^+$  form). The coeff. of variation is 0.1% for 10%, 0.06% for 12.5%, and 0.05% for 15% of B, respectively. The time required is  $< 2$  hr. *Procedure*—Sinter the sample (0.5 g) with ZnO (1 g) and  $Na_2CO_3$  (2 g); dissolve in water and filter through sintered glass. Make the filtrate acid to methyl red and set aside *in vacuo* for 3 min. Stir with the resin (2 ml), filter through paper and dilute the filtrate to 250 ml. Neutralise an aliquot (100 ml) with NaOH soln. to methyl red, add mannitol (7 g) and titrate with 0.067 N NaOH to phenolphthalein. Correct the figure according to the B content (e.g., deduct 0.20 ml of 0.067 N NaOH for 2%, 0.12 ml for 6%, and 0.04 ml for  $> 12\%$  of B). K. SAITO

**4154. Determination of boron in beryllium, zirconium, thorium and uranium. Dissolution in bromine-methanol.** A. R. Eberle and M. W. Lerner (New Brunswick Lab., U.S. Atomic Energy Commission, New Brunswick, N.J.). *Anal. Chem.*, 1960, **32** (2), 146-149.—Boron, in metals which dissolve in bromine-methanol, is determined at 525  $m\mu$  after colour development with diamino-chrysazin (4:5-diamino-1:8-dihydroxyanthraquinone) (I) (Cogbill and Yoe, *Anal. Abstr.*, 1958, **5**, 796). Beryllium scavenger is added after dissolution of the metal to remove excess of Br. Distil the boron ester into water, add a suspension of  $Ca(OH)_2$  and evaporate to dryness. Develop the colour for 30 to 60 min. with I. Determine the extinction at 525  $m\mu$ . Read the content of B from a calibration curve. A new calibration is necessary for each batch of I. The results are erratic below 0.2  $\mu g$ . The standard deviation of 15 determina-

tions on Zircaloy is  $\pm 0.00058$  on a mean of 0.0243%. Although  $F^-$  interfere with the colour the amount normally present does not affect the results. The procedure can be adapted to many other metals. R. M. S. HALL

**4155. The polarography of aluminium.** G. F. Reynolds (Ministry of Supply, Royal Arsenal, Woolwich, London). *Z. anal. Chem.*, 1960, **173** (1), 24-29 (in English).—A summary of work by the author on the Solochrome Violet RS (C.I. Mordant Violet 5) - Al reaction (*Anal. Abstr.*, 1959, **6**, 867; 1955) is given. T. R. ANDREW

**4156. Rapid determination of aluminium content by high-frequency titration.** E. Pungor and E. E. Zapp (Inst. de Chim. Min. et Anal., Univ. "L. Eötvös", Budapest, Hungary). *Bull. Soc. Chim. France*, 1960, (1), 121-124.—This is a French version of a paper published, in English, in *Egypt. J. Chem.*, 1959, **2** (1), 81; cf. *Anal. Abstr.*, 1960, **7**, 911. E. J. H. BIRCH

**4157. Rapid determination of aluminium in cracking catalysts by a modified Wänninen and Ringbom method.** A. Elo, jun., and J. R. Polky (Catalyst Div., Nalco Chem. Co., 4001 West 71st St., Chicago 29, Ill.). *Anal. Chem.*, 1960, **32** (2), 294-295.—The modification of the original method (cf. *Anal. Abstr.*, 1955, **2**, 2360) is to adjust the pH to 3 before complexing the Al with EDTA. After adding EDTA, buffer to pH 4.5, add ethanol and back-titrate as in the original method. The sample need not then be boiled and a smaller excess of EDTA can be used. Several ions interfere but only Fe need be considered in cracking catalysts. This is determined separately colorimetrically and subtracted from the apparent aluminium. Polyphosphate interferes but can be hydrolysed. The standard deviation (120 results, 3 analysts) for 13.14% of  $Al_2O_3$  is  $\pm 0.047$ . Gravimetric results (37) gave 13.20% and  $\pm 0.19$ . R. M. S. HALL

**4158. Aluminium determination in reactor cooling water.** J. F. Emery and G. W. Leddicotte (Oak Ridge National Lab., Tenn.). *U.S. Atomic Energy Comm.*, Rep. CF-58-9-20, Sept., 1958, 3 pp.—A method for the determination of sub-microgram amounts of Al in reactor cooling water by neutron activation analysis is described.

NUCL. SCI. ABSTR.

**4159. Analysis and composition of aluminium corrosion products.** H. P. Godard and W. E. Cooke. *Corrosion*, 1960, **16**, 117-123.—Methods reported in this Technical Committee Report of the Nat. Ass. Corrosion Engrs include X-ray diffraction, X-ray fluorescence, differential thermal analysis, electrographic methods, spectrographic analysis, microscopical examination and quant. and qual. tests. Analytical results are presented in 17 tables. A study is made of corrosion products in fresh water, sea water and in the atmosphere.

LIGHT METALS BULL.

**4160. Silicon in aluminium and aluminium alloys (perchloric acid method).** British Standards Institution (2 Park Street, London, W.1.). B.S. 1728: Part 11: 1960. 7 pp.—The Si is converted to insol.  $SiO_2$  by the dissolution of the metal in NaOH soln. followed by evaporation with  $H_2O_2$  and fuming with excess of  $HClO_4$ . If Sn and Sb are present they are volatilised as bromides. After filtration the  $SiO_2$  is determined by the usual treatment with  $H_2SO_4$  and HF. N. E.

**4161. Determination of traces of cadmium in aluminium.** Shikao Hashimoto and Reizi Tanaka (Sumitomo Metal Ind., Ltd., Sennen-cho, Minatoku, Nagoya). *Japan Analyst*, 1959, **8** (9), 564-568.—Cadmium in aluminium metal is extracted with dithizone (**I**) in  $\text{CHCl}_3$  and determined photometrically at 517  $\mu$ . There is no interference from Ag, Bi, Sn, Ni (< 10 mg each),  $\text{Fe}^{II}$  (< 7.5 mg),  $\text{Fe}^{III}$ , Cu, Cr (< 5 mg each), or Mn (< 2 mg). *Procedure*—Dissolve the sample (1 g) in NaOH soln. (20%) (28 ml) containing tartaric acid soln. (20%) (10 ml) and KCN soln. (1%) (5 ml), add hydroxyammonium chloride soln. (**II**) (10%) (2 ml), dilute to 70 ml and shake with **I** in  $\text{CHCl}_3$  (0.008%, w/v) (15 and 10 ml). Shake the  $\text{CHCl}_3$  layer with tartaric acid soln. (20%) (25 ml), wash with  $\text{CHCl}_3$  (5 ml), add **II** soln. (10%) (0.5 ml), NaOH soln. (20%) (18 ml) and KCN soln. (0.5%) (1 ml), cool and shake with **I** in  $\text{CHCl}_3$  (0.008%, w/v) (15 ml) for photometry. K. SAITO

**4162. Colour reaction for gallium.** V. K. Kuznetsova and N. A. Tananaev. *Nauch. Dokl. Vyssh. Shkol. Khim. i Khim. Tekhnol.*, 1959, (2), 289-292; *Ref. Zhur., Khim.*, 1959, (24), Abstr. No. 86,097.—The detection and photometric determination of Ga is based on the formation, in 6 N HCl, of a complex with Brilliant green (**I**). The complex is easily extracted with benzene as a green soln.; the presence of  $\text{Al}^{3+}$  favours the extraction. To detect Ga, to 1 ml of soln. (6 N in HCl) add 0.5 ml of a 0.5% soln. of **I** in 6 N HCl (or of a 1% ethanolic soln.) and extract with benzene (2 ml). No interference in the detection is caused by the presence of alkali metals, alkaline-earth metals, Al, In, Ti, Zr, W, Cr, Mo, U, Mn, Co, Ni, Cu, Zn, Cd, Hg, Pb, As, Bi, Se, Te, Rh, Pd, Ru, Pt, Nb or Ta; large amounts of W, Ag,  $\text{Hg}^I$ , Ir,  $\text{Sn}^{II}$  and F interfere;  $\text{Fe}^{III}$ ,  $\text{Sb}^V$ ,  $\text{Ti}^{III}$  and  $\text{Au}^{III}$  are first reduced with  $\text{TiCl}_3$  soln. The method can be used to determine Ga in nephelites, coal ash, sulphide minerals and bauxites. For the photometric determination of Ga in metallic aluminium, dissolve 1 g of sample in 6 N HCl, and make up to 50 ml with water and HCl to give a final soln. 6 N in HCl; to 2 ml of the resulting soln. add a few drops of a 10 to 20% soln. of  $\text{TiCl}_3$  and the same vol. of HCl (sp.gr. 1.19), add 0.5 ml of a 0.5% soln. of **I** in 6 N HCl, dilute to 3 ml with 6 N HCl, extract with 3 ml of benzene, set aside for 10 or 15 min. and measure the extinction with a red filter. C. D. KOPKIN

**4163. Colour and fluorescence reactions for gallium.** I. M. Korenman, F. R. Sheyanova and S. D. Kunshin (N. I. Lobachevsky Gorky State Univ.). *Zhur. Anal. Khim.*, 1960, **15** (1), 36-42.—Nine dyes have been investigated for their use as sensitive reagents for Ga. All the dyes have hydroxyl groups in the *oo*-positions to the azo group. Some of the dyes form coloured as well as fluorescent reaction products. The compound of Ga with gallion [8-amino-2-(3-chloro-2-hydroxy-5-nitrophenylazo)-1-naphthol-3-sulphonic acid] has been studied. A. BURWOOD-SMITH

**4164. New reagent for the luminescence determination of gallium.** A. M. Lukin and E. A. Bozhevol'nov (All-Union Sci. Res. Inst. of Chem. Reagents, Moscow). *Zhur. Anal. Khim.*, 1960, **15** (1), 43-48.—The luminescence of compounds of Ga with trihydroxyazo reagents obtained by combining resorcinol with diazo compounds of *o*-aminophenol and its derivatives has been investigated. The most useful reagent for the determination of

Ga is 5-chloro-2:2':4'-trihydroxyazobenzene-3-sulphonic acid. At pH 2.0 to 3.0 the fluorescence is not hindered in the presence of Li, Na, K, Cs,  $\text{NH}_4^+$ , Ag, Zn, Cd, Hg, Be, Mg, Ca, Sr, Ba, Ti, In, Ge, Pb, As,  $\text{Sb}^{III}$ ,  $\text{Sb}^{IV}$ , Bi, Cr, Se, Te, Mn, Ru, Co, Th, Nd, Ce, Pr, Ni, Cl $^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ , phthalates, citrates or acetates at concn. of 50  $\mu$ g in 5 ml; Sn, Zr and Pd do not interfere at concn. < 5  $\mu$ g in 5 ml, and Cu,  $\text{Fe}^{III}$ ,  $\text{Fe}^{II}$ , V and Mo at concn. < 0.5  $\mu$ g in 5 ml. The reagent has been used in the determination of  $1.9 \times 10^{-4}$  % of Ga in selenium and errors did not exceed 15%. A. BURWOOD-SMITH

**4165. Separation of gallium from other elements by the formation of an amalgam.** V. I. Lysenko and E. V. Lisitsyna. *Zavod. Lab.*, 1960, **26** (2), 145-147.—To determine Ga in aluminium, the sample (0.5 to 3 g) is dissolved in 80 to 100 ml of 8.5 N NaOH and the insol. matter is filtered off and washed with 20 to 25 ml of 8.5 N NaOH. The soln. is treated with 10 to 15 ml of 0.5% sodium amalgam at 55° to 60° and vigorously stirred during 60 min. The amalgam is separated and washed with water and then decomposed electrolytically in 50 to 100 ml of 2 to 3 N  $\text{H}_2\text{SO}_4$  at 50° with an anodic c.d. of 2 amp. per sq. cm. When the potential becomes + 0.56 V vs. the S.C.E. the soln. is removed and Ga is determined therein colorimetrically or polarographically. Instead of electrolytic decomposition the amalgam can be treated at 60° to 70° with 6 N HCl.

G. S. SMITH

**4166. Separation of gallium from zinc in ammonium carbonate solution by means of an ionite.** I. P. Alimarin, E. P. Tsintsevich and A. N. Gorokhova (M. V. Lomonosov Moscow State Univ.). *Zavod. Lab.*, 1960, **26** (2), 144-145.—From a soln. 2 M in ammonium carbonate, Ga (1 part) can be completely separated from Zn (1 to 10 parts) by passage through a column (0.8 cm  $\times$  35 cm) containing 8 to 10 g of the anionite EDE-10P ( $\text{CO}_3^{2-}$  form). The Ga is then eluted by means of 2.5 N HCl. With from 100 to 1000 parts of Zn per 1 part of Ga the soln. should be treated with aq.  $\text{NH}_3$  to give a pH of between 9 and 10. For the separation of large amounts of Ga (1000 to 10,000 parts) from small amounts of Zn (1 part) the soln. 2 M in ammonium carbonate is passed through a column of the cationite KU-2 ( $\text{NH}_4^+$  form). Gallium is not adsorbed.

G. S. SMITH

**4167. Separation of indium and gallium by means of diethyldithiocarbamate.** A. I. Busev, T. N. Zholondkovskaya and Z. M. Kuznetsova (M. V. Lomonosov Moscow State Univ.). *Zhur. Anal. Khim.*, 1960, **15** (1), 49-50.—Gallium diethyldithiocarbamate (**I**) is pptd. at pH 1 to 8.5 and quantitatively at pH 2.7 to 5.0. At pH 1.5 to 5, **I** is quantitatively extracted with ethyl acetate. Pptn. and extraction are not influenced by the presence of tartaric and sulphosalicylic acids, but oxalic acid interferes. Indium diethyldithiocarbamate (**II**) is quantitatively pptd. and extracted with ethyl acetate at pH 3 to 10. Tartaric, sulphosalicylic and oxalic acids do not interfere. The method for separating In and Ga is based on the pptn. of **II** or on its extraction with ethyl acetate at pH 3 to 5 in the presence of excess of oxalate. The error for In and Ga is  $\pm 3\%$  at In to Ga ratios from 2:1 to 1:10. *Procedure*—To a soln. containing 2 to 6 mg of In and 2.5 to 30 mg of Ga add 20 to 30 mg of Na oxalate per mg of metal. Neutralise with aq.  $\text{NH}_3$  and add 2% aq. Na diethyldithiocarbamate soln. The soln. containing **II** is set aside for 8 to 24 hr.,



then filtered, and the **II** is washed with water and dried at 105°. The conversion factor for In is 0.205. Gallium is pptd. from the filtrate and washings with 8-hydroxyquinoline.

A. BURWOOD-SMITH

**4168. The determination of indium and gallium with morin.** A. I. Busev and E. P. Shkrobot. *Vestn. Moskov. Univ.*, 1959, (4), 199-206.—Morin (3:5:7:2':4'-pentahydroxyflavone) is used in the determination of small quantities of In and Ga by both spectrophotometric and fluorescence methods. The fluorescence method is more sensitive and is used in the range 0.005 to 1  $\mu$ g in 10 ml for In and 0.01 to 0.05  $\mu$ g in 10 ml for Ga with errors  $\pm$  20%. An acetate buffer at pH 3.6 is used and a concn. of morin of  $4.4 \times 10^{-5}$  M. Optimum concn. for the spectrophotometric method are 10 to 70  $\mu$ g in 10 ml for In and 3 to 15  $\mu$ g in 10 ml for Ga.

A. BURWOOD-SMITH

**4169. Photometric titration of indium by the use of an indirect indicator.** Toyokichi Kitagawa (Fac. of Educ., Kobe Univ., Sumiyoshi, Higashinada-ku). *Japan Analyst*, 1959, **8** (9), 594-596.—The end-point for the EDTA titration of In (Flaschka and Abdine, *Anal. Abstr.*, 1957, **4**, 361) becomes sharper in chloroacetate buffer of pH 2.5 to 2.7 by the use of a Cu-EDTA complex (0.1 M, 2 drops) and 1-(2-pyridylazo)-2-naphthol (PAN) soln. (0.1%, in methanol) (a few drops) in the presence of 10% dioxan. K. SAITO

**4170. Direct complexometric titration of indium with 4-(2-pyridylazo)resorcinol as indicator.** A. I. Busev and N. A. Kanaev. *Nauch. Dokl. Vyssh. Shkol'y. Khim. i Khim. Tekhnol.*, 1959, (2), 299-301; *Ref. Zhur., Khim.*, 1959, (24), Abstr. No. 86,098.—Neutralise 20 or 25 ml of indium nitrate or sulphate soln. with N NaOH to an opalescence, add 3 ml of conc. acetic acid (to pH 2.3 or 2.5) and 1 or 2 drops of 0.1% aq. soln. of 4-(2-pyridylazo)-resorcinol (PAR) (I), warm to between 60° and 70° and titrate with EDTA (disodium salt) soln. till the colour changes from pink to yellow; in the presence of large amounts of Na acetate (pH > 3) the colour change is not clear. Under the above titration conditions, 2.2 to 83.7  $\mu$ g of In was titrated with an error  $\pm$  0.3%. No interference is caused by the presence of Al, Cd, Zn, Mg, Mn and Ca. The soln. of I is stable for a year.

C. D. KOPKIN

**4171. Radioactivation analysis of indium by the use of a radium - beryllium neutron source.** Yuzuru Kusaka (Fac. of Sci., Konan Univ., Higashinada-ku, Kobe). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1959, **80** (12), 1419-1422.—The radioactivation determination of In (> 0.05%) in zinc is carried out with the aid of a Ra-Be source (50 mC of Ra) without separation. A well-type NaI scintillator is much superior to a Geiger-Müller counter. The determination of In by the resonance neutron absorption method (1.458 eV) is less accurate.

K. SAITO

**4172. Analysis of pure metals. Determination of lead and zinc impurities in indium and thallium.** V. A. Nazarenko, N. A. Fuga, G. V. Flyantikova and K. A. Esterlis (Inst. of Gen. and Inorg. Chem., Acad. Sci., UkrSSR). *Zavod. Lab.*, 1960, **26** (2), 131-135.—*Procedure for lead*—Standards for the spectrographic determination of Pb in samples containing from 0.03 to 0.00025% are made by

mixing PbSO<sub>4</sub> with SrSO<sub>4</sub> [which has been prepared Pb-free by mixing boiling soln. of Sr(NO<sub>3</sub>)<sub>2</sub> and K<sub>2</sub>SO<sub>4</sub> and filtering] and then adding an equal wt. of carbon powder containing 0.5% of Bi<sub>2</sub>O<sub>3</sub> to serve as an internal standard. For samples of indium, 1 g is dissolved in 10 ml of water and 1 ml of conc. H<sub>2</sub>SO<sub>4</sub> and the hot diluted soln. (100 ml) is treated with 1 ml of Sr(NO<sub>3</sub>)<sub>2</sub> soln. containing 20 mg of Sr and 2 ml of 5% K<sub>2</sub>SO<sub>4</sub> soln. The soln. is kept hot for 1 hr. and then set aside for 12 hr. The ppt. is washed with dil. H<sub>2</sub>SO<sub>4</sub> and ethanol and ignited at 600° to 650°, then mixed with carbon powder and excited in a Sventitskil activated arc at 8 amp. The lines Pb 2833.07 Å and Bi 2993.3 Å are measured. For thallium samples, 1 g is dissolved in 4 ml of water and 2 ml of conc. HNO<sub>3</sub>, the soln. is evaporated to dryness, the residue is dissolved in 10 ml of water, 2 ml of a saturated soln. of SO<sub>2</sub> is added and the diluted (100 ml) and boiling soln. is treated with 1 ml of the Sr(NO<sub>3</sub>)<sub>2</sub> soln. and 4 ml of the K<sub>2</sub>SO<sub>4</sub> soln. The subsequent procedure is as described above. *Procedure for zinc*—For samples of indium, 1 g is dissolved in 6 ml of conc. HCl, then 20 ml of water and 4 g of tartaric acid are added and the cooled soln. is treated with 3 ml of 2% KSCN soln. and neutralised to bromocresol purple with 20% NaOH soln. and dil. H<sub>2</sub>SO<sub>4</sub> (1:4). After addition of 10 ml of an acetate buffer soln. (pH 5), the soln. is extracted with pyridine-CHCl<sub>3</sub> (1:20) (3  $\times$  5 ml). The extracts are washed with 15 ml of 2.5% KSCN soln. and evaporated to dryness; the residue is treated with 0.2 ml of conc. H<sub>2</sub>SO<sub>4</sub>, 0.2 ml of conc. HNO<sub>3</sub> and 0.2 ml of 2% K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> soln. and evaporated to dryness; the residue is ignited and dissolved in 5 ml of water, 0.1 ml of 5% NaOH soln. and then 5 ml of a 0.01% soln. of dithione in CHCl<sub>3</sub> are added, and the Zn is determined photometrically at 530 m $\mu$ . For samples of thallium, 1 g is heated with 1 ml of conc. HNO<sub>3</sub> and 2 ml of water, 1 ml of conc. H<sub>2</sub>SO<sub>4</sub> and 5 ml of water are added, and the soln. is evaporated to fuming, followed by addition of 5 ml of water and re-evaporation. Addition of water and evaporation is repeated four times. The residue is dissolved in 100 ml of water and the soln. is electrolysed in a platinum dish (anode) at 4.5 V and 2.5 to 3 amp. with a platinum-gauze cathode. The Tl-free soln. is evaporated to a vol. of 60 ml and boiled with 5 ml of saturated SO<sub>2</sub> soln. The cooled soln. is mixed with a further 5 ml of SO<sub>2</sub> soln. and then with 3 ml of 25% KSCN soln. and subsequently treated as described above. The methods are applicable to the determination of 10<sup>-5</sup>% of Pb or 5  $\times$  10<sup>-5</sup>% of Zn. G. S. SMITH

**4173. Anion exchange of radio-isotopes of indium, tin and antimony and the preparation of carrier-free indium-113m and antimony-125.** I. Stronński and W. N. Rybakow (Inst. of Nuclear Research, Cracow). *Chem. Anal., Warsaw*, 1959, **4** (5-6), 877-882.—The use of the strong anion exchanger ASD-2 permits the separation of trace amounts of the radio-isotopes of In, Sb and Sn. The resin was synthesised from polystyrene and trimethylene-diamine. The resin suspension (diam. of particles  $\approx$  30  $\mu$ ) in 3 N HCl was formed into a column of 100 mm in height and 2 mm in diam., and washed with 2.5 ml of conc. HCl (containing 10 to 20 mg of Br per ml) and finally with 3 N HCl until the washings were colourless. Correct washing with 3 N HCl is essential for the successful separation of In and Sb. Then 0.1 ml of a soln. of Sn in 3 N HCl, (activity 5.5  $\times$  10<sup>5</sup> counts per min., concn. 2.3 mg of Sn<sup>IV</sup> per ml) was placed on the column. Isotopes

of Sb and In were eluted with 1.6 ml of 3 N HCl and Sn with 1 ml of 2 N HClO<sub>4</sub>. The rate of elution, regulated by pressure, was  $\approx 0.04$  ml per 0.3 sq. cm per min. This method makes possible the preparation of carrier-free <sup>115m</sup>In and <sup>125</sup>Sb. The same column can be repeatedly used for the preparation of radiochemically pure <sup>115m</sup>In.

L. SMAKOWSKI

**4174. Quantitative determination of scandium with the use of mandelic acid.** I. P. Alimarin and Han-Si Shen (M. V. Lomonosov Moscow State Univ.). *Zhur. Anal. Khim.*, 1960, **15** (1), 31-35.—The pptn. of H<sub>2</sub>[Sc(C<sub>6</sub>H<sub>5</sub>O<sub>2</sub>)<sub>2</sub>].nH<sub>2</sub>O (I) with mandelic acid is carried out in a soln. of pH 2 to 3, and under these conditions rare-earth elements and Th are not pptd. I dissolves in aq. NH<sub>3</sub> to give (NH<sub>4</sub>)<sub>3</sub>[Sc(C<sub>6</sub>H<sub>5</sub>O<sub>2</sub>)<sub>2</sub>], and Sc is determined by titrating I with 0.092 N aq. NH<sub>3</sub> and back-titrating with 0.1 N HCl. Errors are  $\pm 2\%$ . I decomposes at 280°.

A. BURWOOD-SMITH

**4175. Quantitative determination of scandium by spectrographic analysis.** V. M. Alekseeva and A. K. Rusanov (All-Union Inst. of Mineral Raw Materials, Moscow). *Zhur. Anal. Khim.*, 1960, **15** (1), 27-30.—Silicate ores are analysed spectrographically for Sc by using mixtures of 0.05 g of the ore with 0.15 g of a powder containing equal parts of SrCO<sub>3</sub> and carbon together with 0.5% by wt. of lanthanum oxide. Analysis is carried out with the line pairs Sc II 4246-83 and La II 4263-58 A, or Sc II 4246-83 and La II 4269-49 A. The range of determination is 0.001 to 0.1%, with a mean error for a single determination of  $\pm 10\%$ .

A. BURWOOD-SMITH

**4176. Paper chromatography of inorganic ions in nitrate solutions. I. Scandium, yttrium, actinium and the lanthanides.** J. Danon and M. C. Levi (Brazilian Centre for Phys. Res., Rio de Janeiro). *J. Chromatography*, 1960, **3** (2), 193-194 (in English).—Descending chromatography of soln. of Sc, Y, Ac and lanthanides in butanol at 25° on a paper previously saturated with 7 M LiNO<sub>3</sub>-2 M HNO<sub>3</sub> is described; R<sub>F</sub> values for La, Y and Sc were 0.40, 0.58 and 1.00. Lanthanum, Ce, Pr and several pairs of non-adjacent lanthanides could be separated; separation of La and Ac was demonstrated by the use of <sup>228</sup>Ac. Rare-earth elements were detected by u.v. irradiation of their 8-hydroxyquinolines.

P. D. FARR-RICHARD

**4177. Colour reactions and paper-chromatographic studies of yttrium and zirconium.** G. Kallistratos, A. Pfau and B. Ossowski (Radio-biochem. Dept., Max-Planck-Inst., Mariensee/Trenthorst, Germany). *Anal. Chim. Acta*, 1960, **22** (2), 195-199.—The sensitivity of the colour reactions of these metals with 22 organic compounds is discussed, and 6 solvent mixtures for the separation of Y from Zr by paper chromatography are tabulated.

E. G. CUMMINS

**4178. Spectrophotometric determination of the rare-earth elements, yttrium and cerium by bromopyrogallol red.** J. Herrington and K. C. Stead (A.W.R.E., Aldermaston, Berks., England). *Anal. Chim. Acta*, 1960, **22** (2), 180-184.—The procedure described has been applied to purified, separated solutions, containing 10 to 50 µg of an element, obtained from ion-exchange columns. The complexes formed by bromopyrogallol red with the rare-earth elements and Y are determined at 665 mµ; that formed with Ce at 675 mµ.

E. G. CUMMINS

**4179. Reduction of lanthanum, praseodymium and neodymium at the dropping-mercury electrode.** Akio Iwase (Fac. of Liberal Arts, Yamagata Univ., Koshirakawa-cho). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1959, **80** (10), 1133-1138.—The current-voltage curve was examined for La, Pr and Nd in tetramethylammonium bromide and LiCl soln. of pH 2 to 6. These trivalent ions give a single wave distinguishable from the hydrogen wave, and the  $E$  vs.  $\log i/(i_d - i)$  curve is linear at pH < 3, whereas the reduction is irreversible at a higher pH. The  $E_0$  shifts towards positive values with rise of pH, but is almost constant at pH > 4 and < 2.5. The diffusion current constant agrees with that calculated from the equivalent conductivity for  $n = 3$ .

K. SAITO

**4180. Isolation of the rare-earth elements, a chlorination-volatilisation procedure.** J. B. Zimmerman and J. C. Ingles (Radioactivity Div., Mines Branch, Dept. of Mines and Tech. Surveys, Ottawa, Canada). *Anal. Chem.*, 1960, **32** (2), 241-246.—The ore (10 to 100 mg of rare earths) is chlorinated at 900°. Most other elements, including Sc and Th, volatilise. The residue is dissolved in 1% aq. HCl, conc. aq. NH<sub>3</sub> is added, and the ppt. is ignited to the oxides. The yield of rare earths is above 90% with a chlorination time  $\approx 30$  min. If the bulk of the ore is U or Th, an extraction with tributyl phosphate-CCl<sub>4</sub> will reduce the bulk before chlorination. The losses in this step are small. Less than 2% of other elements is typically found in the oxides.

R. M. S. HALL

**4181. Separation of the rare-earth elements of the cerium group with cation-exchange resin and zinc-EDTA complex.** Seizo Misumi and Tomitsugu Taketatsu (Chem. Dept., Fac. of Sci., Kyushu Univ., Hakozaki, Fukuoka). *Japan Analyst*, 1959, **8** (10), 673-675.—By the use of the Zn-EDTA complex, having a pK value intermediate between those of the La and Ce complexes, the fractionation of La, Ce, Pr, Nd and Sm is greatly improved, the separation factor ( $D$ ) at pH 4.5 being 3 for Ce and Pr and 15 for Ce and Sm.  $D = [\text{Ce (mole \%)} \text{ in the resin/Pr or Sm (mole \%)} \text{ in the resin}]/[\text{Ce (mole \%)} \text{ in the percolate/Pr or Sm (mole \%)} \text{ in the percolate}]$ .

K. SAITO

**4182. Separation of total rare earths and thorium from some multiple-oxide minerals.** J. R. Butler and R. A. Hall (Dept. of Geology, Imperial College of Sci. and Technol., London). *Analyst*, 1960, **85**, 149-150.—Chlorine, bubbled through SCl<sub>2</sub> at 40° to 50°, is passed through a silica tube enclosed in a furnace and containing the mineral in a silica boat. The furnace temp. is raised to 500° (550° for some minerals) and kept at that temp. for 1 hr. Titanium, Nb and Ta begin to volatilise at 400° to 430°, and condense in a flask containing 10% HNO<sub>3</sub>. A pale-yellow sublimate collects in the tube outside the furnace and, at a higher temp., Fe forms a red-brown film nearer the furnace. The residue in the boat contains all the Na, Mg, Al, Si, K, Ca, Sc, Sr, Y, Ba, La and Th, and may contain some Fe. Uranium is divided between the residue and the yellow sublimate. If the mineral contains no Na or K the residue can be dissolved in HNO<sub>3</sub> and treated with dil. HF to precipitate fluorides of the alkaline-earth metals, scandium, the rare-earth metals and thorium. Rare-earth metals with Th can be separated from these fluorides after dissolution in HClO<sub>4</sub> and pptn. with methyl oxalate.

A. O. JONES



4183. Spectrographic determination of mixtures of rare-earth elements in samarium and europium. V. L. Kustas and G. V. Lazebnaya. *Zhur. Anal. Khim.*, 1960, 15 (1), 57-60.—A method is described for the quantitative determination of rare-earth elements in samarium and europium oxides. Two series of standards are prepared from pure rare-earth-metal oxides, one each for the cerium and yttrium groups. The line pairs used are listed. Determinations are possible in the range 0.01 to 4% for Sm and 0.002 to 5% for Eu. The mean relative error is 3 to 5% and the minimum sample size is 5 to 10 mg. A. BURWOOD-SMITH

4184. Coulometric determination of small concentrations of carbon dioxide in gas mixtures. J. Prosz and I. Hegedüs-Wein (Inst. f. anorg. Chem., Techn. Univ., Budapest). *Period. Polytech.*, 1960, 4 (1), 1-7 (in German).—An apparatus is described consisting of a Ba(OH)<sub>2</sub>-impregnated filter-paper, between two annular silver electrodes. The paper is treated with phenolphthalein and exposed in the apparatus to the gas stream. After completion of the exposure, the time for disappearance of the red colour, while passing current through the paper, is recorded. The technique is suitable for 0.04 to 1% of CO<sub>2</sub>. T. R. ANDREW

4185. Mass-spectrometric analysis of oxygen in carbon monoxide and carbon dioxide. I. Lauder (Univ. Brisbane, Queensland). *Aust. J. Chem.*, 1959, 12, 630-636.—Results of measurements of <sup>18</sup>O abundances in CO and CO<sub>2</sub> by using a Nier-type isotope-ratio mass spectrometer are given. Carbon monoxide is a far superior gas to CO<sub>2</sub> as a carrier for the oxygen isotopes because of the more rapid pump-out and the almost complete absence of memory in the mass spectrometer. The slight variation of the measured ratio with output voltage is attributed mainly to the non-ohmic response of the grid resistors to the electrometer valves. NUCL. SCI. ABSTR.

4186. Studies on chemical luminescence analysis. II. Chemical behaviour of cyanide ions towards the chemiluminescence of luminol [3-aminophthalhydrazide] and the determination of cyanide ion by measurement of the induction period. Soichiro Musha, Mitsuo Ito, Yoshiziro Yamamoto and Yoshihiro Inamori (Fac. of Engng, Osaka Prefectural Univ., Sakai). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1959, 80 (11), 1285-1288.—Further examination of the inhibiting action of CN<sup>-</sup> on the chemiluminescence of luminol (I) with H<sub>2</sub>O<sub>2</sub> in the presence of Cu<sup>2+</sup> (Weber et al., *Ber.*, B, 1942, 75, 2051) showed that the induction period increases with increase in concn. of CN<sup>-</sup>, and the log of the induction period is proportional to the concn. of CN<sup>-</sup> (< 12 p.p.m.). The sample soln. is mixed with I soln. (0.1% in 0.04 M aq. NH<sub>3</sub> containing 0.7% of NH<sub>4</sub>Cl) (10 ml) and CuSO<sub>4</sub> soln. (100 p.p.m.) (1 ml), the mixture is added to H<sub>2</sub>O<sub>2</sub> soln. (0.20%) (1 ml) and the time taken for the product to attain a certain intensity of fluorescence is measured. The presence of Fe<sup>3+</sup> (> 5 p.p.m.), NO<sub>3</sub><sup>-</sup> (> 0.4), I<sup>-</sup> (> 20) and SO<sub>4</sub><sup>2-</sup> (> 0.5) causes interference. This method is applicable to sea water and industrial waste water. K. SAITO

4187. Colorimetric determination of silicon in the presence of phosphorus. J. Paul and W. F. R. Pover (Dept. of Med. Biochem. and Pharmacol., Univ., Birmingham, England). *Anal. Chim. Acta*, 1960, 22 (2), 185-189.—The test soln. (2 ml), an

aq. soln. such as human or rat urine, is shaken in a 50-ml separating-funnel with N HCl (2 ml) and then 5% ammonium molybdate soln. (4 ml) is added and the shaking is continued for 3 min. (The pH of this soln. is 1.0.) The selective removal of the molybdophosphate by a single extraction with 20 ml of ethyl acetate for 30 sec. follows. The aq. phase is then treated with 30% sodium sulphite soln. (4 ml) and its extinction is measured after 25 min. against an extracted blank. The eight experiments reported, in which microgram amounts of Si, ranging from 7 to 69 µg per ml, have been determined, each in the presence of 1 mg of sodium phosphate, show a mean error of + 2.1%. E. G. CUMMINS

4188. The polarography of molybdosilicic acid. H. Hahn and K. Grasshoff (Inst. f. anorg. Chem. Univ., Kiel, Germany). *Z. anal. Chem.*, 1960, 173 (1), 29-35 (in German).—The effect, on the polarographic reduction of molybdosilicic acid, of varying the temperature, pH, and MoO<sub>4</sub><sup>2-</sup> to Si ratio, is reported and a procedure described for the determination of Si in aluminium and aluminium alloys. After dissolution of the sample (0.1 g) in NaOH soln. any Fe<sup>II</sup> is oxidised with H<sub>2</sub>O<sub>2</sub>, the pH is adjusted to 1.4 with HCl, ammonium molybdate is added and the soln. is diluted to 100 ml. A 25-ml aliquot is transferred to a 50-ml flask, 10 ml of ethyl methyl ketone is added and, after 1 hr., 5 ml of 0.1% Pril soln. (an arylalkylsulphonate, Böhmche Fettchemie) is added and the whole diluted to 50 ml with a citrate buffer (pH 2.5). Under these conditions the E<sub>1</sub> for molybdosilicic acid is between -0.35 and -0.40 V vs. the S.C.E. Results for known additions of from 50 to 500 µg of Si show recoveries of 96 to 104%. T. R. ANDREW

4189. Determination of germanium in zinc ore products. Z. Gregorowicz (Dept. of Inorg. Chem., Silesian Polytech. Inst., Gliwice, Poland). *Chem. Anal., Warsaw*, 1959, 4 (5-6), 829-835.—2:3:7-Trihydroxy-9-phenyl-6-fluorone was used for colorimetric determinations of Ge in samples obtained from zinc manufacture. The samples were fused with NaOH and Na<sub>2</sub>O<sub>2</sub> and the Ge was extracted with CCl<sub>4</sub> from soln. in 8 N HCl. Other elements present in zinc blends do not interfere. The method was suitable for the determination of 2.5 to 25 µg of Ge per 25 ml. The mean coeff. of variation (24 determinations on 4 different samples) was 6.1% for Ge contents of 5 to 25 p.p.m. L. SMAKOWSKI

4190. Photometric determination of germanium with benzopyrylium compounds. L. I. Kononenko and N. S. Poluëktov (Inst. of Gen. and Inorg. Chem., Acad. Sci., Ukrainian SSR, Odessa). *Zhur. Anal. Khim.*, 1960, 15 (1), 61-68.—The reaction of Ge with four kinds of o-dihydroxybenzopyrylium compound has been studied. The most sensitive reaction is given by 6:7-dihydroxy-2:4-diphenylbenzopyrylium chloride; in an acid medium (0.1 N HCl) the yellow colour changes to orange-red. By using 6:7-dihydroxy-2:4-diphenylbenzopyryran (I) it is possible to determine 25 µg of Ge in 10 ml of soln. The ratio between the number of the reagent molecules and the Ge atoms in the colour complexes is 2:1. Procedure.—Into a 25-ml flask put 1 ml of 5 N HCl, 0.2 to 0.3 ml of H<sub>3</sub>PO<sub>4</sub> (1:1), 2 to 3 drops of H<sub>2</sub>O<sub>2</sub> and 2 ml of 5% EDTA soln., then 1 ml of 1% gelatin and 1.25 ml of 0.2% ethanolic I. Make up to the mark with water and after 3 min. measure the extinction. Permissible concn. (per 25 ml of soln.)

of foreign elements are—12.5 mg of Bi, 2.5 mg of Th, 1.5 mg of Fe<sup>III</sup>, 1.0 mg of Ti, 0.75 mg of Al, 0.5 mg of Zr, 1 mg of Hf, 0.4 mg of Sn<sup>II</sup>, 100 µg of V, 40 µg of Nb, 30 µg of Ta, 20 µg of Sn<sup>IV</sup>, 15 µg of W, 5 µg of Mo and 5 µg of Sb. A. BURWOOD-SMITH

**4191. Polarographic determination of tin in the presence of lead. Application of the extraction with ammonium thiocyanate.** Genkichi Nakagawa (Dept. of Ind. Chem., Nagoya Inst. Tech., Gokisocho, Showa-ku). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1959, **80** (11), 1288-1290.—The extraction of Sn (< 15 mg) with ethyl ether (30 ml) in the presence of Pb (< 50 mg) is best carried out from N HCl (30 ml) containing 2 M NH<sub>4</sub>SCN, and the small amount of Pb (< 0.3 mg) in the ether layer is removed by shaking with N HCl containing M NH<sub>4</sub>SCN. The ethereal soln. is heated with conc. H<sub>2</sub>SO<sub>4</sub> (5 ml) and conc. HNO<sub>3</sub> (5 to 10 ml) until white fumes appear, then made up to 100 ml with NH<sub>4</sub>Cl (21 g), gelatin soln. (0.1%) (5 ml) and water, and the polarogram is recorded. The second wave of Sn is suitable for quant. analysis. This method is applicable to the analysis of copper alloys, Cu being removed as CuSCN. K. SAITO

**4192. Determination of copper and lead in crude tin by alternating-current polarography.** Kamihiro Itsuki and Teru Kaji (Osaka Refinery, Mitsubishi Metal & Mining Co., Shinkawasaki-cho). *Japan Analyst.*, 1959, **8** (9), 568-571.—Tin is removed with HBr and Br, and Pb and Cu (< 1%) are determined by a.c. polarography (applied potential, 20 mV) in 0.45 N HClO<sub>4</sub>. Other metal ions, including Bi (< 1 mg), Sb (< 2), As (< 2), Zn (< 3), Fe (< 3) and the small amount of remaining Sn (< 20), do not interfere with the polarography. K. SAITO

**4193. Ultra-violet spectrophotometric determination of lead in hydrobromic acid.** Yuroku Yamamoto (Chem. Dept., Fac. of Sci., Kyoto Univ., Sakyo-ku). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1959, **80** (12), 1426-1428.—Lead in HBr of concn. < 0.8 N gives an absorption max. at 290 to 303 mµ which shifts towards longer wavelength with increase in HBr concn. until, at > 5 N HBr, it reaches 302 mµ. The extinction coeff. also increases with increase in HBr concn., but the working curve is linear up to 12 p.p.m. of Pb in 4.3 N HBr. Interference results from Fe, Sn, Sb, Bi (> 10 p.p.m. each), and Ni, Co, Mn, Al and As<sup>V</sup> (each in > 20-fold excess). K. SAITO

**4194. Use of aluminium hydroxide and barium carbonate as carrier for lead in the presence of copper.** Masanori Sato (Chem. Dept., Fac. Sci., Kyoto Univ., Sakyo-ku). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1959, **80** (12), 1453-1456.—Less than 1 mg of Pb is quant. co-pptd. with BaCO<sub>3</sub> (> 50-fold molar excess of Ba). The pptn. of BaCO<sub>3</sub> becomes rapid in the presence of Al(OH)<sub>3</sub> (≈ 5 times the molar concn. of Pb), and the co-pptn. of Cu (< 1 g) is < 5%, but Cu can be almost completely removed by re-pptn. The Pb (> 0.002% in copper) is polarographically determined in N HCl containing 0.01% of polyacrylamide; there is no interference from Al or Ba. K. SAITO

**4195. Determination of traces of lead in high-purity metals.** Tadashi Yanagihara, Nobuhisa Matano and Akira Kawase (Nat. Res. Inst. for Metals, Naka-meguro, Meguro-ku, Tokyo). *Japan Analyst.*, 1959, **8** (9), 576-582.—Lead (< 10 µg) in metallic nickel, magnesium, copper, zinc or silver is co-pptd. with BaCrO<sub>4</sub> in NH<sub>4</sub>ClO<sub>4</sub> soln. of pH 7

to 10, the Cr is removed as CrO<sub>2</sub>Cl<sub>2</sub> and the Pb is determined polarographically or photometrically. The presence of Cl<sup>-</sup> and NO<sub>3</sub><sup>-</sup> vitiate the co-pptn. *Procedure*—Dissolve the sample (< 2 g) in HNO<sub>3</sub> (1:1) (≈ 20 ml), heat to white fumes with HClO<sub>4</sub> (20 ml), dissolve the residue in water (150 ml), add 7% K<sub>2</sub>CrO<sub>4</sub> soln. (2 ml), make ammoniacal, add 4% BaCl<sub>2</sub> soln. (2 ml) and filter. Dissolve the ppt. in HClO<sub>4</sub> (1:1) (10 ml), heat to white fumes, add HCl (1 ml) and heat nearly to dryness. Determine the Pb by the dithizone method or polarographically. K. SAITO

**4196. Simple method for the determination of barium, calcium and sodium in lead alloys.** J. Sedzimir, A. Gaj and K. Kubisz (Dept. of Phys. Chem. and Electro-Chem., Sch. of Mining and Metallurgy, Cracow). *Chem. Anal., Warsaw*, 1959, **4** (5-6), 869-875.—Different methods for the analysis of lead-barium (calcium)-sodium alloys are discussed. The main difficulty arises from the fact that very large amounts of Pb (> 90%) must be separated from other constituents, and the application of the Cl<sup>-</sup>-H<sub>2</sub>S method of separation was found to be satisfactory for these alloys. After the separation of Pb, Ba and Ca were determined in the residual soln. by standard methods. For the determination of Na, the procedure advocated is evaporation of the sample with H<sub>2</sub>SO<sub>4</sub>, after the removal of Pb, Ba and Ca, followed by titration with standard NaOH soln., with phenolphthalein as indicator, to neutralise NaHSO<sub>4</sub> and the excess of H<sub>2</sub>SO<sub>4</sub>. The amount of sulphate was then determined gravimetrically. In this way the Na content of the sample may be determined. The small percentage error for Na indicates the particular suitability of this method. L. SMAKOWSKI

**4197. Ammonium benzene- and naphthalene-seleninates as reagents for the quantitative determination of titanium.** V. S. Sotnikov and I. P. Alimarin. *Nauch. Dokl. Vyssh. Shkol'y. Khim. i Khim. Tekhnol.*, 1959, (2), 296-298; *Ref. Zhur., Khim.*, 1959, (24), Abstr. No. 86,108.—It is shown that in acid medium ammonium benzeneseleninate (I) and ammonium naphthaleneseleninate (II) precipitate Ti<sup>4+</sup> as TiO(C<sub>6</sub>H<sub>5</sub>SeO<sub>2</sub>)<sub>2</sub> and TiO(C<sub>10</sub>H<sub>7</sub>SeO<sub>2</sub>)<sub>2</sub>, respectively; these compounds are soluble in conc. acids. The sensitivity of the reaction for Ti is 1 in 7.5 × 10<sup>4</sup> for I and 1 in 10<sup>4</sup> for II. On this basis a method is developed for the gravimetric determination of Ti in the presence of the rare-earth elements and Al, Be and Fe; the product is weighed as TiO<sub>2</sub>. To the soln. of Ti<sup>4+</sup> add 7 ml of 10 N HNO<sub>3</sub>, dilute to 100 ml (for pptn. with I soln.) or 200 ml (for pptn. with II soln.), heat to between 70° and 80° and add the reagent. Heat for 20 to 30 min. and add paper pulp. Cool, filter through a thick paper, wash the ppt. with 1% HNO<sub>3</sub> containing 1% of I or 0.5% of II, ignite at between 800° and 900° to TiO<sub>2</sub> and weigh. In the presence of Al, Fe, Be and the rare-earth elements, wash the ppt. with a little water, dissolve it by warming with 7 ml of 10 N HNO<sub>3</sub>, and precipitate Ti as above. The error in determining Ti is ± 0.3%. No interference is caused by the presence of Cu, Ag, Be, Mg, Ca, Sr, Ba, Zn, Cd, Al, Mn, Co or Ni; Sn, Zr, Nb, Ta, Mo and W interfere. The method can be used to determine Ti in alloys and ores. C. D. KOPKIN

**4198. Polarographic behaviour of quadrivalent titanium in ascorbic acid as basal electrolyte and its determination in the presence of much trivalent iron and other ions.** P. Szarvas and A. Gergely

(Kossuth Lajos Tudományegyetem Szervetlen- és Anal.-Kém. Intézet, Debrecen, Hungary). *Magyar Kém. Foly.*, 1960, **86** (2), 61-66.—The polarographic behaviour of  $Ti^{IV}$  as a function of the pH has been examined in *N* ascorbic acid as supporting electrolyte. The values of  $E_1$  and of the diffusion current change with pH, but the diffusion current is approx. constant between pH 1.25 and 2.25. In the presence of  $Fe^{III}$  the wave of  $Ti^{IV}$  cannot be determined above pH 2. At pH 1.5,  $Ti^{IV}$  (5 to 25 g per ml) can be determined in the presence of a 100-fold amount of  $Fe^{III}$  and a 5-fold amount each of  $Co^{III}$ ,  $Mn^{II}$  and  $Ni^{II}$ . At pH 1.5, when a soln. containing 20 g of  $Ti^{IV}$  per ml in the final dilution is used, the following ions do not interfere—a 150-fold wt. of  $Fe^{III}$ ,  $Fe^{II}$ ,  $Co^{II}$  and  $Mn^{II}$ , a 25-fold wt. of  $Cr^{III}$ , and a large excess (e.g., 25 mg per ml) of  $Cl^-$  or  $SO_4^{2-}$ . The proportion of  $V^{V}$  and  $W^{VI}$  to  $Ti^{IV}$  should not exceed 1:1. Any amount of  $Mo^{VI}$  interferes. A 5-fold amount of  $PO_4^{3-}$  does not interfere if a 100-fold excess of  $Fe^{III}$  is also present. The advantages of this method are that  $Fe^{III}$  need not be removed, and that no separate reducing agent is needed. The accuracy is the same as is usual in polarographic analysis. A. G. PETO

4199. Gas-chromatographic separation of metal halides by inorganic fused salt substrates. R. S. Juvet and F. M. Wachi (Dept. Chem. and Chem. Engng, Univ. Illinois, Urbana, U.S.A.). *Anal. Chem.*, 1960, **32** (2), 290-291.—A mixture containing  $TiCl_4$  saturated with  $SbCl_5$  is separated (retention times 2.0 and 12.0 min.) on a  $BiCl_3$ - $PbCl_2$  eutectic column (Johns-Manville C-22 firebrick support) at  $240^\circ$  with *N* as carrier gas. A 12-ft. long borosilicate-glass column is used. R. M. S. HALL

4200. Polarographic determination of titanium in titanium-organosilicon compounds. E. A. Terent'eva and M. O. Korshun. *Khim. Nauka i Prom.*, 1959, **4** (3), 415-416; *Ref. Zhur.*, *Khim.*, 1959, (24), Abstr. No. 86,109.—To the sample (containing 2 to 10 mg of Ti) add 1.5 ml of HF (1:5), evaporate and repeat the evaporation. Add about 3 ml of conc.  $H_2SO_4$  to the residue, evaporate to fumes of  $SO_3$  and dilute with 70%  $H_2SO_4$  to 100 ml; filter if carbon forms. To 30 ml of the resulting soln. add 6 drops of 1% gelatin soln., pass *N* for 15 min. and polarograph with a dropping-mercury cathode; the  $E_1$  is 0.37 V v. the S.C.E. Construct a calibration curve for the range  $10^{-5}$  to  $10^{-4}$  M Ti from samples of metallic titanium. C. D. KOPKIN

4201. Determination of titanium, tantalum and niobium in carbide mixtures (containing tungsten). V. G. Shcherbakov and Z. K. Stegendo. *Zavod. Lab.*, 1960, **26** (2), 139-142.—*Procedure for Ti*—The sample (0.20 g) is dissolved in 10 ml of  $H_2SO_4$  and 5 g of  $(NH_4)_2SO_4$ , 75 ml of 10% oxalic acid soln. and 75 ml of water are added and the hot soln. is treated with 25% aq.  $NH_3$  (10 ml in excess) to precipitate Ti and Ta. The ppt. is collected and washed with hot water containing a few drops of aq.  $NH_3$  and is then dissolved in 30 ml of dil.  $H_2SO_4$  (1:4). The soln. is diluted to 100 ml and treated with amalgamated zinc, and Ti is determined by titration with  $Fe^{3+}$  soln. in the presence of  $NH_4SCN$  soln. as indicator. *Procedure for Ta*—The washed ppt., containing Ti and Ta, obtained as described above, is dissolved in 7 ml of dil.  $H_2SO_4$  (1:4), and the cooled soln. is diluted to 200 ml and treated with 10 ml of a 10% soln. of 5:6-benzoquinoline (I) in ethanol. The heated soln. is

treated after 3 to 4 min. with 1 ml of 15%  $H_2O_2$  soln. and set aside for 4 hr. The ppt. is collected and washed 8 to 10 times with a soln. containing 2 ml of  $H_2SO_4$  and 4 ml of 10% I soln. in 1 litre, then dried and ignited. The ppt. is dissolved in  $H_2SO_4$  and  $(NH_4)_2SO_4$ , the soln. is diluted to 100 ml and Ta is pptd. with aq.  $NH_3$ . The washed ppt. is ignited and weighed. G. S. SMITH

4202. Analytical chemistry of zirconium. A review. G. W. C. Milner and J. W. Edwards (Anal. Chem. Group, A.E.R.E., Harwell, Berks., England). *Analyst*, 1960, **85**, 86-97.—Methods of separation by pptn. with inorganic and organic reagents, ion exchange, solvent extraction and chromatography are noted. Methods of determination include gravimetric methods by pptn. with mandelic acid or its derivatives, and by tartrazine, and pptn. as phosphate, arsenate or basic selenite. Volumetric methods include those with EDTA used as titrant directly or indirectly. Absorptiometric methods are reviewed and also a few miscellaneous methods, some involving radioactivation. (139 references.) A. O. JONES

4203. Volumetric determination of zirconium. I. Permanganate method. A. Schneer and H. Hartmann (Inst. for General and Inorg. Chem., L. Eötvös Univ., Budapest). *Acta Chim. Acad. Sci. Hung.*, 1960, **22** (1), 35-49.—This is a German version of a paper published in Hungarian, in *Magyar Kém. Foly.*, 1959, **65**, 31; cf. *Anal. Abstr.*, 1959, **6**, 3444. J. H. WATON

4204. Complexometric determination of zirconium. V. F. Luk'yanov and E. M. Knyazeva. *Zhur. Anal. Khim.*, 1960, **15** (1), 69-72.—Ores, cakes and concentrates containing 2 to 40% of Zr were satisfactorily analysed by the following method. *Procedure*—Fuse 0.1 to 0.2 g of sample with 1 to 3 g of  $KHF_2$  in a platinum crucible. Cool, add 15 to 20 ml of conc.  $H_2SO_4$  and heat on a sand bath until fumes appear. Cool, and transfer the soln. to a 300-ml flask. Proceed as in (a) (see below) in the presence of  $Zn^{2+}$ ,  $Al^{3+}$ ,  $Fe^{2+}$ ,  $Sn^{2+}$ ,  $Sn^{4+}$ ,  $VO_3^-$ ,  $CrO_4^{2-}$ ,  $MoO_4^{2-}$ ,  $WO_4^{2-}$  or  $PO_4^{3-}$ , or as in (b) in the presence of  $Zn^{2+}$ ,  $Cd^{2+}$ ,  $Cu^{2+}$ ,  $Co^{2+}$  or  $Ni^{2+}$  (or  $Ti^{4+}$ ,  $> 15$  mg), but in the absence of  $PO_4^{3-}$ . (a) To the  $H_2SO_4$  soln. add cold 20%  $NaOH$  soln. until zirconium hydroxide is pptd. and then a further 5 to 10 ml. The total volume should be less than 200 ml. The ppt. is collected on a coarse paper and washed 6 to 8 times with 5%  $NaOH$  soln. then re-dissolved with hot 2 N  $HCl$ , and the vol. is reduced to 100 ml. Boil for 2 to 3 min., add ascorbic acid to reduce  $Fe^{3+}$  and 0.05 M EDTA. Boil for 2 to 3 min., cool to room temp. and add 1 to 2 drops of 2:4-dinitrophenol soln. (1% ethanolic); add aq.  $NH_3$  until a bright-yellow colour appears, then add  $HCl$  (1:2) dropwise until the colour is discharged (pH 2.3 to 2.4). Add 6 to 8 drops of 1% aq. arsenazo soln. and back-titrate the EDTA with thorium nitrate soln. until the bright-pink colour changes to blue-violet. (b) To the  $H_2SO_4$  soln. add 1.5 to 3 ml of 30%  $H_2O_2$  in the cold and 25% aq.  $NH_3$  until zirconium hydroxide is pptd. and then add a further 3 to 5 ml. Collect the ppt. on a coarse paper and wash it 6 to 8 times with 2%  $NH_4Cl$  and a little aq.  $NH_3$  and  $H_2O_2$ . Re-dissolve the ppt. with hot 2 N  $HCl$  and then proceed as in (a). Errors are  $< \pm 0.6\%$ . A. BURWOOD-SMITH

4205. Determination of zirconium(IV) with tartrazine by a polarographic titration method. G. Popa, D. Negoiu, and G. Baiulescu (Anal. Chem. Lab., Univ. "C. I. Parhon", Bucharest, Romania). *Anal. Chim. Acta*, 1960, **22** (2), 200-202.—Tartrazine is added as reagent to the zirconium soln. in a polarographic cell at  $-0.9$  V. An amperometric end-point is obtained when excess of tartrazine appears. E. G. CUMMINS

4206. Determination of zirconium by the use of the polarogram of cadmium. Akio Iwase (Fac. of Liberal Arts, Yamagata Univ., Koshirakawa-cho). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1959, **80** (10), 1142-1145.—The formation of the Zr-EDTA and Zr-CyDTA complexes was measured polarographically with the aid of Cu-EDTA; the values for  $\log K$  were 18.0 and 21.8, respectively. The substitution of  $Zr^{4+}$  for Cd in Cd-EDTA is accelerated by  $NH_4SCN$  and the amount of  $Cd^{2+}$  liberated is almost constant if the molar concn. of Cd-EDTA is  $> 4$  times that of the Zr at pH 4 to 5. The sample soln. is mixed with  $NH_4SCN$ , Cd-EDTA and gelatin soln. to produce, respectively, 1 M, 20 mM and 0.01% soln.; these are buffered with acetate and the height of the wave due to Cd is measured. K. SAITO

4207. Polarographic determination of trace amounts of lead in zirconium and its alloys. D. F. Wood and H. A. Nicholls (Res. Dept., I.C.I. Ltd., Metals Div., Kynoch Works, Witton, Birmingham, England). *Analyst*, 1960, **85**, 139-144.—The sample is dissolved in dil.  $H_2SO_4$  and fluoroboric acid, the soln. is oxidised with  $HNO_3$ , boiled and cooled. It is then treated with citric acid soln. and aq.  $NH_3$  (2 ml in excess of neutrality), and when cold with KCN soln. and Na diethyldithiocarbamate soln., and then extracted with  $CHCl_3$ . The extract is evaporated and the residue is evaporated with  $HNO_3$  and  $HClO_4$ . This residue is dissolved in dil.  $HNO_3$  (1:99), the soln. is transferred to a polarographic cell, argon is bubbled through and the polarogram is developed with a start potential of  $-0.5$  V against the mercury-pool anode. The peak potential for lead under these conditions is  $-0.76$  V. The lead content is calculated by reference to the wave heights found for control soln. The standard deviation at the 40-p.p.m. level is  $\approx 1.5$  p.p.m. A. O. JONES

4208. Determination of chromium in zirconium metal and Zircaloy-2. U.K.A.E.A. (Research Group, Harwell, Berks.). Report AERE-AM 63, 3 pp.—The sample is dissolved in HF which is then removed by fuming with  $H_2SO_4$ . After oxidation with  $KMnO_4$ , diphenylcarbazide is added and the extinction of the soln. is measured in a Spekker absorptiometer with an Ilford 605 filter. The method has been written in its present form by P. T. S. Sandon. N. E.

4209. Spectrographic determination of hafnium to zirconium ratios. G. Rossi (Lab. CISE, Milan, Italy). *Spectrochim. Acta*, 1960, **16** (1-2), 25-29.—Full experimental details are given for the d.c. arc spectrographic determination of hafnium in zirconium. A mixture of the oxides with graphite and barium fluoride (4:1:1) was the most satisfactory. A 20-amp. d.c. discharge is used, the exposure (with a rotating sector) extending from 20 to 50 sec. after the commencement of arcing for the most constant results. For 0.1 to 10% of Hf the line-pair Hf II 2641.4 - Zr II 2856.06 is used and

for 1 to 50% the line-pair Hf I 2779.36 - Zr I 2792.04 may be used. R. M. S. HALL

4210. Volumetric determination of thorium with potassium ferrocyanide in the presence of *o*-dianisidine. H. Basińska and K. Przybyszewska (Dept. of Inorg. Chem., Copernicus Univ., Toruń). *Chem. Anal., Warsaw*, 1959, **4** (5-6), 791-793.—Thorium ions are titrated with standard soln. of  $K_4Fe(CN)_6$ , with *o*-dianisidine as a redox indicator. The colour change at the end-point is from pink to green. Small amounts of acetic acid,  $HNO_3$ , or ethanol do not influence the titration. The method cannot be applied to the determination of metals which form ferrocyanides of very low solubility. The error of determination as compared with that by a potentiometric method is  $< 1\%$ . L. SMAKOWSKI

4211. Turbidimetric titration of thorium with standard ammonium oxalate solution. Sumio Komatsu, Kazuo Taki and Minoru Takada (Fac. of Liberal Arts, Toyama Univ., Toyama). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1959, **80** (9), 1070-1071.—The extinction at 420  $m\mu$  of the turbid soln. obtained by the titration of  $Th^{IV}$  soln. (1 to 7 mg per 50 ml, 10 N in acetic acid) with 0.01 N oxalic acid reaches a max. at the end-point in the presence of poly(vinyl alcohol) (0.2% soln., 10 ml per 50 ml). K. SAITO

4212. Determination of microgram quantities of thorium in silicate rocks, sediments, and other materials after enrichment of thorium by means of ion exchange. J. Korkisch and P. Antal (Anal. Inst., Univ., Vienna, Austria). *Z. anal. Chem.*, 1960, **173** (2), 126-138 (in German).—Enrichment of Th on Dowex 50 ( $H^+$  form) and removal of interfering Ti and Zr by elution with citric acid permit spectrophotometric evaluation of Th (about 20  $\mu g$ ) by the thoron method with 95 to 97% recoveries. The method is applicable to the analysis of minerals. *Procedure*—Fuse the rock (0.5 to 1 g) with  $Na_2CO_3$  (5 to 10 times its wt.) in a platinum crucible. Dissolve the melt in HCl and precipitate  $SiO_2$  by repeated evaporation with HCl. Take up in 4 N HCl (20 ml), filter, and wash with 0.5 N HCl (25 ml) and remove the Si with HF- $HNO_3$ . Dissolve the residue in 4 N HCl (2 ml) and add the soln. to the filtrate obtained above. Dilute to 1 litre. Reduce  $Fe^{III}$  completely to  $Fe^{II}$  with ascorbic acid (I) and pass the soln. through Dowex 50 ( $H^+$  form). Wash with N HCl containing I (until the percolate is free from Fe), then with 0.1 M citric acid (free from Ti) and finally with water (2  $\times$  20 ml). Elute the Th with 6 N  $H_2SO_4$  (50 ml), evaporate to dryness, and dissolve in 0.1 N HCl. Add 0.1% thoron soln. (1 ml) and dilute to 10 ml with 0.1 N HCl. Determine the extinction at 545  $m\mu$  and compare with a calibration curve. J. P. STERN

4213. Titration of traces of ammonia after Kjeldahl distillation. O. I. Milner and R. J. Zahner (Socony Mobil Oil Co., Paulsboro, N.J., U.S.A.). *Anal. Chem.*, 1960, **32** (2), 294.—An acidimetric finish is now proposed instead of the earlier colorimetric finish (Milner *et al.*, *Ibid.*, 1958, **30**, 1528). Sulphamic acid (0.01 N primary standard) is used with boric acid in the ammonia distillation receiver. The indicator is methyl red - alphasaurin (C.I. Acid Blue 9). The recovery of ammonia with the low concn. of boric acid proposed averages 99.97% (5 determinations). R. M. S. HALL



4214. Ultra-violet determination of nitrogen dioxide as nitrite ion. A. P. Aitshuller and A. F. Wartburg (Air Pollution Engng Res., Robert A. Taft Sanitary Engng Center, U.S. Department of Health, Education and Welfare, Cincinnati 26, Ohio). *Anal. Chem.*, 1960, **32** (2), 174-177.—Nitrogen dioxide (0.01 to 10%) in nitrogen is determined at 355 m $\mu$  after conversion into nitrite by absorption in aq. caustic alkali soln. Collection in bubblers gave  $3.38 \pm 0.13\%$  on 8 determinations; collection in sampling flasks by various methods gave  $3.35 \pm 0.3\%$  on 14 determinations. Gravimetric results are somewhat lower, but are complicated by water-loss corrections. R. M. S. HALL

4215. Spectrophotometric determination of nitrous acid with disodium 7-amino-8-(4-amino-2-sulphophenylazo)-1-naphthol-3-sulphonate. Yukiteru Katsube and J. H. Yoe (Tech. Inst., Himeji, Japan). *Bull. Chem. Soc. Japan*, 1960, **33** (2), 190-194.—The method has a sensitivity of 1 in  $10^4$ . Beer's law is obeyed up to  $\approx 2$  p.p.m. of nitrous acid;  $\text{As}^{3+}$ ,  $\text{Br}^-$ ,  $\text{Fe}^{3+}$ ,  $\text{Ce}^{3+}$ ,  $\text{CeO}_4^{2-}$ ,  $\text{F}^-$ ,  $\text{Hg}^+$ ,  $\text{Hg}^{2+}$ ,  $\text{I}^-$ ,  $\text{Mn}^{2+}$ ,  $\text{MnO}_4^-$ ,  $\text{MoO}_4^{2-}$ ,  $\text{Sn}^{2+}$ ,  $\text{Sn}^{4+}$ ,  $\text{Ti}^{4+}$  and  $\text{Zr}^{4+}$  interfere. The interference of  $\text{Fe}^{3+}$  is eliminated with EDTA. I. JONES

4216. Determination of phosphoric acid. X. Spectrophotometric determination of a micro amount of phosphoric acid by solvent extraction as molybdophosphate. Masayoshi Ishibashi and Masayuki Tabushi (Fac. of Sci., Kyoto Univ., Sakyo-ku, Kyoto). *Japan Analyst*, 1959, **8** (9), 588-593.—The use of butyl acetate (I) for the extraction of molybdophosphate (Wadelin and Mellon, *Anal. Abstr.*, 1954, **1**, 679) was radiochemically re-examined with  $^{32}\text{P}$ . Arsenic, oxalic, tartaric and citric acids ( $> 10$  mg each) interfere with the photometry at 310 m $\mu$ . The extraction is facilitated by increasing the concn. of  $\text{HCl}$  and  $\text{MoO}_4^{2-}$  (e.g.,  $> 95\%$  from 0.5 N  $\text{HCl}$  containing 0.5% of  $\text{Na}_2\text{MoO}_4$ ). The working curve is linear for  $< 3$   $\mu\text{g}$  of  $\text{P}_2\text{O}_5$  per ml. K. SAITO

4217. Colorimetric determination of orthophosphate in the presence of condensed phosphate. Krishna Kumar Tewari and P. S. Krishnan (Chem. Dept., Lucknow Univ., India). *Anal. Chim. Acta*, 1960, **22** (2), 111-117.—Investigation of the direct colorimetric method of Lowry and Lopez (*cf. J. Biol. Chem.*, 1946, **162**, 421) has shown that the presence of pyrophosphate, tri- and tetra-phosphate or polymetaphosphates inhibits the development of the orthophosphate colour, whereas cyclic metaphosphates have no effect. The presence of the dialysate of polymetaphosphates, in which the concn. of condensed phosphates is low, also has no effect. The inhibition by polymetaphosphate is partly overcome by storing the coloured soln. for about 90 min.; after this period the colour develops no further. It was found that the presence of  $\text{Cu}^{II}$ ,  $\text{Ni}^{III}$ ,  $\text{Fe}^{II}$  and  $\text{Fe}^{III}$  generally neutralised the inhibiting effect of the polymetaphosphate and specifically changed the colour-development time. None of the metaphosphates interferes in the estimation of orthophosphate by the isobutyl alcohol extraction method of Berenblum and Chain (*cf. Biochem. J.*, 1938, **32**, 295). E. G. CUMMINS

4218. Modifications to the bromide-distillation method for determining arsenic. I. Hoffman and M. Rowsome (Anal. Chem. Res. Service, Res. Branch, Dept. of Agric., Ottawa, Canada). *Analyst*, 1960, **85**, 151-152.—In this modification of the

method of Bartlett *et al.* (*Brit. Abstr. C*, 1953, 134) the prescribed procedure is followed to the point at which the distillate is transferred through the top of the trap to a beaker, but 3 ml of the specified  $\text{KBr}$  soln. is added through the dropping-funnel instead of 2 ml. Three rinsings of the trap with 2-ml portions of water are added to the distillate, which is then neutralised with  $\text{NaOH}$  soln. The colour is formed by addition of 3 ml of  $\text{N HCl}$ , ammonium molybdate and aq. hydrazine sulphate soln., and the extinction is measured at 840 m $\mu$ . Quoted results show that, for the best recovery, sample aliquots should contain  $\approx 15$   $\mu\text{g}$  of  $\text{As}$ . A. O. JONES

4219. Potentiometric titration of antimony(III) and arsenic(III) with iodine solution. Kozo Uno and Tetsuhei Tachikawa (Chem. Sect., Univ. of Engng, Muroran). *Japan Analyst*, 1959, **8** (9), 572-576.—Potentiometric titration was satisfactory with 0.01 to 0.1 N iodine soln., with the use of a platinum-silver electrode in a bicarbonate soln. Satisfactory results were obtained for 3 to 300 mg of  $\text{Sb}$  in the presence of tartrate and 1.2 to 120 mg of  $\text{As}$  per 50 ml. K. SAITO

4220. Photometric determination of antimony in zinc electrolytes and alloys. P. N. Kovalenko and N. P. Moricheva. *Izv. Vyssh. Uchebn. Zavedenii. Khim i Khim. Tekhnol.*, 1959, **2** (3), 322-327; *Ref. Zhur.*, *Khim.*, 1959, (24), Abstr. No 86,189.—The influence of the components of zinc electrolytes and alloys on the accuracy of the photometric determination of  $\text{Sb}$  with methyl violet is studied. It is shown that salts of  $\text{Cu}$ ,  $\text{Ni}$ ,  $\text{Cd}$  and  $\text{Mn}$  in low concn. in a zinc electrolyte do not interfere in the determination of small amounts of  $\text{Sb}$  by this method. Zinc salts, even in large amounts, do not noticeably affect the accuracy of determining  $\text{Sb}$ . Iron does not interfere at concn. up to 10 mg in 50 ml of soln.; with larger amounts of  $\text{Fe}$ , the concn. of  $\text{HCl}$  and  $\text{KNO}_3$  must be increased to ensure complete extraction of the antimony complex from the aq. soln. with benzene. The methyl violet method also gives satisfactory results in determining small and relatively large amounts of  $\text{Sb}$  in non-ferrous alloys; the error of the determination is  $> 5\%$ . C. D. KOPKIN

4221. Application of trihydroxyfluorone derivatives for the colorimetric determination of trivalent antimony. Ming-Lien Lu, Ta-Chun Liu, I-I Yen and Wei-Kau King (Dept. of Pharm., First Med. Coll., Shanghai). *Acta Chim. Sinica*, 1959, **25** (6), 353-359.—The colour reactions of 13 2:6:7-trihydroxyfluorone derivatives with 73 inorganic ions are studied. In neutral and 0.1 N  $\text{H}_2\text{SO}_4$  soln., all reagents form orange or cherry-red ppt. with  $\text{Sb}^{III}$ ,  $\text{Ge}^{IV}$ ,  $\text{Bi}^{III}$ ,  $\text{Sn}^{II}$ ,  $\text{Sn}^{IV}$ ,  $\text{Fe}^{II}$ ,  $\text{Hg}^+$ ,  $\text{Hg}^{II}$ ,  $\text{In}^{III}$ ,  $\text{Zr}^{IV}$ ,  $\text{VO}_5^-$ ,  $\text{MoO}_4^{2-}$  and  $\text{WO}_4^{2-}$ . The reaction is particularly sensitive to  $\text{Sb}$ ,  $\text{Sn}$  and  $\text{Ge}$ . Investigation is specially directed to  $\text{Sb}$ . In 0.05 to 0.1 N  $\text{H}_2\text{SO}_4$ , 9-diethylaminophenyltrihydroxyfluorone (I) and 9-m-nitrophenyltrihydroxyfluorone (II) produce clear and stable coloured soln. with  $\text{Sb}^{3+}$ . The effect of varying the acidity and temp. on the colour reaction, and interference by some inorganic ions are examined. Beer's law is obeyed over the ranges 0.02 to 0.9  $\mu\text{g}$  of  $\text{Sb}$  per ml and 0.06 to 2  $\mu\text{g}$  of  $\text{Sb}$  per ml for I and II, respectively. Recovery tests show that the error is  $\pm 20\%$  at  $< 0.1$   $\mu\text{g}$  of  $\text{Sb}$  per ml and  $\pm 5\%$  at 0.1 to 0.8  $\mu\text{g}$  of  $\text{Sb}$ . The atomic ratio of  $\text{Sb}$  to I or II in the complex formed

is 1:1. The chelating constants of Sb with I and II are  $5.4 \times 10^{-7}$  and  $1.8 \times 10^{-12}$ , respectively.

S. H. YUEN

**4222. Colorimetric determination of antimony in chromium-nickel alloys.** L. S. Nadezhina. *Trudy Leningr. Politekh. Inst.*, 1959, (201), 120-126; *Ref. Zhur., Khim.*, 1959, (24), Abstr. No. 86,188.—The spectrophotometric characteristics of the coloured complex of Sb with methyl violet in a benzene layer are studied, and its composition is established. The influence of various ions and the acidity of the medium on the photometric determination of Sb with methyl violet is examined. A rapid method is developed for the determination of trace amounts of Sb in chromium-nickel alloys without preliminary concentration and separation of Sb from the main components. The sensitivity of the method is 0.002% on a sample of 0.5 g.

C. D. KOPKIN

**4223. Ultra-violet spectrophotometric determination of bismuth with sulphuric acid.** Yuroku Yamamoto (Chem. Dept., Fac. of Sci., Kyoto Univ., Sakyo-ku). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1959, 80 (11), 1256-1260.—Soln. of Bi in  $H_2SO_4$  absorb at  $< 260 m\mu$  (max. 225 to 232  $m\mu$ ) and the max. shifts towards longer wavelength with increase in concn. of  $H_2SO_4$ . The extinction coeff. decreases with increase in  $H_2SO_4$  concn. up to 10 N and increases in more concentrated acid. The working curve is linear for  $< 30$  p.p.m. of Bi in 1-8 N  $H_2SO_4$ , and for  $< 90$  p.p.m. by the differential method. The error is  $\approx 1\%$ ; changes in temp. and time have little effect on the results. There is significant interference from  $Fe^{III}$  and  $SbV$ .

K. SAITO

**4224. Spectrophotometric determination of vanadium as tungstovanadic acid.** G. W. Wallace and M. G. Mellon (Purdue Univ., Lafayette, Ind., U.S.A.). *Anal. Chem.*, 1960, 32 (2), 204-207.—Aq. sodium tungstate soln. is added to a soln. (pH 2) containing the V to be determined. The extinction at 392  $m\mu$  is measured against tungstate as reference soln. The V content is read from a calibration curve. The colour takes 30 min. to develop and is stable for 24 hr. The optimum pH range is 1.7 to 3.0; at higher values the wavelength of max. absorption is changed. Chromium interferes and must be removed; Fe interferes but can be complexed with fluoride; Pb, Bi, Ba and Ag precipitate the anions and must be removed; silicate interferes by increasing the extinction. The standard deviation is typically  $\pm 0.022$  for 0.97% of V in steel.

R. M. S. HALL

**4225. Determination of trace amounts of vanadium by means of the colour reaction with benzohydroxamic acid.** H. Waleđziak, K. Gorczyńska and D. Ciecierska-Stokłosa (Dept. of Tech. Physics, Inst. of Gen. Chem., Warsaw). *Chem. Anal., Warsaw*, 1959, 4 (5-6), 883-891.—By the method described, 1 to 4  $\mu g$  of V in 25 ml can be accurately determined. The optimum conditions are a 500-fold molar excess of reagent at pH 2.5. It was found that 100-fold amounts of  $Ag^+$ ,  $Pt^{4+}$ ,  $Pb^{2+}$ ,  $Mn^{2+}$  and  $Ni^{2+}$  and 10-fold amounts of  $Al^{3+}$  had only a slight effect on the determination of V, producing an error of  $< 5.0\%$  as compared with an error of  $\approx 3.0\%$  with pure standard soln. The absorption curve of the complex of Al with benzohydroxamic acid at pH 2.5 is given, together with those of the Fe and Ti complexes at pH  $< 2$ , 2.5, 5, 7.5 and 9. It is advisable to separate these metals before determining V.

L. SMAKOWSKI

**4226. Method of "replacing extinction coefficients" in the spectrophotometric analysis of binary mixtures. I. Application for determining traces of metals by means of colour reactions.**

D. Ciecierska-Stokłosa, K. Gorczyńska, J. Świętosławska and H. Waleđziak (Dept. of Tech. Physics, Inst. of Gen. Chem., Warsaw). *Chem. Anal., Warsaw*, 1959, 4 (5-6), 803-809.—A mathematical development of a new spectrophotometric method is described. It is based on colour reactions and may be applied (i) when there is no possibility under the given experimental conditions to exploit analytical wavelengths suitable for attaining satisfactory accuracy, (ii) when it is impossible to determine the two components successively by masking by forming colourless complexes, (iii) when the complex-forming agent is colourless, and (iv) when such a large excess of reagent is used that all cations in the solution form coloured complexes independently of pH, temp., or time parameters. Two general systems of equations are given. The method was applied to the determination of trace amounts of V and Fe with benzohydroxamic acid. The application of the method requires precise determination of the extinction coeff.

**II. Determination of trace amounts of vanadium and iron by the colour reaction with benzohydroxamic acid.** K. Gorczyńska, H. Waleđziak and D. Ciecierska-Stokłosa, *Ibid.*, 1959, 4 (5-6), 809-819.—A method for determination of trace amounts of vanadium and iron in their mixtures was developed on the basis of colour reaction with benzohydroxamic acid. The sum of both components was also determined. The method of "replacing extinction coefficients" was used (Ciecierska-Stokłosa *et al.*, Part I, above) with the following system of equations—

$$A_{gt} - A_{ht} = c_V(a_{Vgt} - a_{Vht}) + c_{Fe}(a_{Fe gt} - a_{Fe ht})$$

$$A_{pr} - A_{qr} = c_V(a_{Vpr} - a_{Vqr}) + c_{Fe}(a_{Fe pr} - a_{Fe qr})$$

where  $A$  = extinction,  $c$  = concn.,  $a_V$  and  $a_{Fe}$  = extinction coeff. of the coloured complexes of V and Fe, subscripts  $g, h, p$  and  $q$  denote wavelengths and  $i, j, r$  and  $s$  = pH values during analysis. Extinction measurements of standard soln. were performed at 385 and 515  $m\mu$  at pH 6.9, 4.2, 2.5 and  $< 2$ . Thus six equations of the type given above were obtained and one equation with extinction coefficients instead of "replacing extinction coefficients." In the concn. range from 1 to 4  $\mu g$  of V plus Fe per ml, the error is  $< 2\%$ . Vanadium and Fe in admixture were determined separately with an error  $< 15\%$ . Results are tabulated and illustrated graphically.

L. SMAKOWSKI

**4227. Determination of small amounts of tantalum and niobium in granite by the isotopic dilution method.** A. P. Savostin and I. P. Alimarin (School of Anal. Chem., Moscow Univ.). *Vestn. Moskov. Univ.*, 1960, (1), 45-48.—By using the radioactive isotopes  $^{182}Ta$  and  $^{95}Nb$ , it is shown that Ta and Nb can be concentrated sufficiently for their determination by moistening 3 to 4 g of the granite with an oxalate soln. of the radioactive isotope of Ta or Nb, decomposing the sample with HF and  $H_2SO_4$ , precipitating the metals from the sulphate soln. with tannin in the presence of ammonium oxalate and EDTA (disodium salt), igniting the ppt., fusing it with  $K_2S_2O_7$  (for Ta) or with  $Na_2CO_3$  (for Nb), and separating Ta or Nb from Ti by the fluoride-pyrogallol method. Titanium is determined with  $H_2O_2$ , and Ta and Nb radio-metrically. Enrichment factors with respect to



Ti of 130 to 260 for Ta and 30 to 130 for Nb are obtained. To determine Ta and Nb, the sample (3 to 4 g) containing the radioactive isotope is decomposed with HF and  $H_2SO_4$ , the metals are separated from Ti by three applications of the fluoride-pyrogallol method, the oxides are fused with  $K_2S_2O_7$  (for Ta) or  $Na_2CO_3$  (for Nb), and the melts are extracted with 10 ml of 0.75 N oxalic acid; Ta is determined in one aliquot of the soln. colorimetrically with rhodamine B, and in another aliquot radiometrically; or Nb is determined colorimetrically with KSCN and radiometrically. Knowing the amount of radioactive isotope added, the contents of Ta and Nb in the granite can then be calculated. Contents of  $5 \times 10^{-4}$  and  $1.8 \times 10^{-4}$  % of Ta and  $6.4 \times 10^{-4}$  and  $2.8 \times 10^{-3}$  % of Nb are determined in this way.

C. D. KOPKIN

**4228. New methods for the determination of very small amounts of ozone.** E. A. Perehud and E. M. Stepanenko (State Sci. Res. Inst. of Work Hygiene and Occupational Diseases, Leningrad). *Zhur. Anal. Khim.*, 1960, 15 (1), 96-98.—Highly sensitive quantitative methods for the determination of ozone are based on extinguishing the luminence of luminol and fluorescein or the change of colour of silica gel saturated with fuchsin soln. The reaction of these indicators with ozone is not affected by up to 6  $\mu$ g of  $NO_2$  per litre. The indicator most sensitive to ozone and inert to  $NO_2$  has a luminol basis.

A. BURWOOD-SMITH

**4229. Determination of polysulphide sulphur in solutions of barium polysulphide and the evaluation of the dependence on time of the formation of the maximum quantity of polysulphide sulphur.** G. Blöckinger (Vysokoj Školy Pedagog., Bratislava, Czechoslovakia). *Chem. Zvesti*, 1960, 14 (1), 32-37.—*Procedure*—To a 250-ml flask add 100 ml of water and 2 g of boric acid and boil for 2 to 3 min. Allow the temperature to fall below boiling-point then add 5 ml of 10% KCN soln. and 5 ml of test soln. (1 g of powdered material in 100 ml of water). Boil for 5 min. and while the soln. is still hot add 3 ml of 5% formaldehyde soln., shake, and set aside for 5 min. Cool to room temp., add 40 ml of satd. bromine water, stopper the flask, and, after 10 min., add 5 ml of 5% phenol soln. and mix thoroughly to remove bromine fumes. Add 1 g of solid KI, allow to react for 15 min. in the stoppered flask, and titrate with 0.1 N  $Na_2S_2O_3$  with starch as indicator; 1 ml of 0.1 N  $Na_2S_2O_3$  = 0.0016 g of polysulphide sulphur. The use of formaldehyde is a safety measure to protect the operator against HCN.

P. G.

**4230. Colorimetric determination of traces of sulphite ions.** Takeshi Kato (Kita College, Osaka Univ., Toyonaka). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1959, 80 (11), 1254-1256.—When methylene blue soln. is mixed with iodine in KI soln. a dark-brown ppt. is obtained, which has the composition  $[C_{16}H_{18}N_3S]I$ . When this compound (30 mg) is added to an aq. soln. (50 ml) containing KI (0.08%) and  $SO_3^{2-}$  buffered with acetate at pH 5.1 to 7.5, iodine is liberated and the extinction at 665  $m\mu$  is proportional to the concn. of  $SO_3^{2-}$  (0.2 to 2 p.p.m.). The reaction is complete within 15 min. and the colour fades gradually. There is interference from Hg,  $Fe^{3+}$  (> 1 p.p.m.), Mn (> 5), Cu (> 5), Ni (> 10),  $CO_3^{2-}$  (> 100),  $NO_3^-$  (> 50), citrate (> 500) and reducing agents. K. SAITO

**4231. Detection of sulphate in a drop by using a glass ring-oven.** H. Balczio and M. Hodos (Anorg. u. Phys.-chem. Inst., Univ. Wien). *Mikrochim. Acta*, 1960, (2), 267-271 (in German).—A filter-paper, previously freed from interfering substances by washing with 0.01% methanolic HCl in the ring-oven, is treated with 0.01 ml of 0.2% aq. Na rhodizonate soln., the oven being at 110°. Aq. NaCl soln. (3%) (0.01 ml) is added, and the salts are washed into the first zone with 0.001% aq. HCl. Aq.  $Ba(NO_3)_2$  soln. (0.2%) (0.02 ml) is added, and this is washed with 0.001% aq. HCl into the first zone where a bright-red Ba rhodizonate-NaCl complex is formed. The excess of  $Ba^{2+}$  is washed into a second zone with 0.01% methanolic HCl. The test soln. is added and washed into the first zone with 0.001% HCl. The paper is removed and the oven is cooled and washed well with ethanol and ethyl ether. The temp. is raised to 70° and the rhodizonate liberated by the sulphate is washed into the second zone with 0.01% methanolic HCl, where it forms a red-brown colour with the  $Ba^{2+}$ . As little as 5  $\mu$ g of  $SO_4^{2-}$  can be detected. H. M.

**4232. Micro-determination of sulphate with lead nitrate as titrant and dithione as indicator.** D. C. White (Res. and Dev. Dept., The Distillers Co. Ltd., Epsom, Surrey, England). *Mikrochim. Acta*, 1960, (2), 282-285 (in English).—The recently described method (*Ibid.*, 1959, 254) has been extended to the direct determination of  $SO_4^{2-}$  in water, and the effects of  $Cl^-$  and  $K^+$  were studied. Only very small amounts of K can be tolerated since, in the presence of amounts approaching the equivalent of the  $SO_4^{2-}$ , the titration reaction near the end-point is very sluggish. Cations are removed by passing the water sample through a column of Amberlite IR-120 in the acid form. The first 30 ml is discarded. To a 5-ml portion of the subsequent percolate is added one drop of 0.1% bromophenol blue soln., and the soln. is adjusted to a yellow-green colour with dilute aq.  $NH_3$  or  $HNO_3$  soln.; 20 ml of acetone containing 0.5% of acetic acid and 0.6 ml of 0.02% dithione soln. in acetone are added and the emerald-green soln. is titrated with 0.01 N  $Pb(NO_3)_2$  to the first red-purple colour. Phosphate and chloride interfere; the former must be removed, as described earlier (*loc. cit.*), and  $Cl^-$  (> 2 mg per 25 ml) should be removed by adding 1 ml of  $HNO_3$  (1:1) to the 5-ml portion of the percolate, evaporating to dryness, adding 1 ml of urea and evaporating to dryness. The residue is dissolved in 2 ml of water and titrated as described above. B. B. BAUMINGER

**4233. Determination of sulphate.** V. Palatý (Dept. of Power Engng, Inst. of Chem. Technol., Prague). *Chem. & Ind.*, 1960, (7), 176—Sulphate is determined by the change of absorption of the thorium complex of a suitable metallochromic indicator (catechol violet, SPADNS, Eriochrome cyanine R or Alizarin red S) when sulphate displaces the indicator from the metal. *Procedure*—To a 100-ml flask are added 25 ml of 0.05 M sulphamate buffer (pH 3.20), 10 ml of  $10^{-4}$  M catechol violet and 10 ml of  $10^{-4}$  M  $Th(NO_3)_4$  prepared with de-mineralised water. The sample (or de-mineralised water for the blank) (50 ml) is added and, after diluting the soln. to vol., the extinction is measured at 557  $m\mu$ . The calibration curve is similarly obtained for 0.5 to 100 p.p.m. of sulphate. Interfering cations are removed by passing the sample

through a cation-exchange resin (acid form), and  $\text{PO}_4^{3-}$  and  $\text{F}^-$  by pptn. with  $\text{La}^{3+}$ .

E. J. H. BIRCH

**4234. Analysis of chlorosulphonic acid.** E. Korinth (Farbwerke Hoechst, A.-G., Frankfurt/Main-Höchst). *Angew. Chem.*, 1960, **72** (3), 108-109.—A procedure that is more precise than previously known methods has been developed for the analysis of chlorosulphonic acid (I) containing only  $\text{H}_2\text{SO}_4$  and HCl as impurities. The free HCl is distilled off at 20° and 40 torr, and the loss in wt. is corrected by Henry's law for the solubility of HCl in I. This gives the proportion of free HCl. The total Cl is then determined gravimetrically on another sample and the proportion of I is calculated;  $\text{H}_2\text{SO}_4$  is then obtained by difference.

G. BURGER

**4235. Polarography of thiocyanate ion. Complex-ion formation with mercury(II) ion.** C. J. Nyman and G. S. Alberts (Dept. of Chem., Washington State Univ., Pullman, U.S.A.). *Anal. Chem.*, 1960, **32** (2), 207-210.—The anodic polarographic oxidation of mercury in soln. of thiocyanate has been investigated over a wide range of concn., and formation constants  $K_2$ ,  $K_3$  and  $K_4$  are reported for the complex ion formed between mercury and thiocyanate.

K. A. PROCTOR

**4236. Micro-determination of selenium with 3:3'-diaminobenzidine.** J. Pien, J. Desirant, F. Orsini and P. Avril. *Ann. Falsif.*, 1960, **53**, 83-91.—The reaction of  $\text{Se}^{IV}$  with 3:3'-diaminobenzidine (I) is used for the colorimetric determination of Se. *General procedure*—To an aliquot ( $> 50 \mu\text{g}$  of Se) add 2.5 M formic acid (2 ml) and 0.1 M EDTA (10 ml) to complex Fe and Cu, etc.; dilute to 50 ml. Adjust the pH to 2 to 3, add an aq. 0.5% soln. of I hydrochloride (2 ml) and allow to stand for 30 to 50 min. Adjust the pH to 6 to 7 with aq.  $\text{NH}_3$ , add 10 ml of toluene and shake for 30 sec. Centrifuge the toluene layer and read the extinction at 420 m $\mu$ . The colour is stable for 5 hr., and Beer's law is followed for 10 to 100  $\mu\text{g}$  of Se in 10 ml of toluene; the sensitivity is 0.05 p.p.m. Not more than 5 mg of V should be present. *For arsenic*—Dissolve a sample in HCl- $\text{HNO}_3$  (1:1), evaporate nearly to dryness and dilute. Proceed as described above. *For stainless steel*—Dissolve the sample (0.5 to 1 g) in HCl- $\text{HNO}_3$  (2:1), evaporate to low vol., dilute and filter. Make up to 250 ml and take an aliquot for determination of Se. Recoveries are 90 to 111%. *For copper*—Dissolve the sample in  $\text{HNO}_3$ - $\text{H}_2\text{O}$  (1:1), evaporate to low vol. and dilute. Add 6.5 g of EDTA per g of sample. *For sulphuric acid*—Dilute and neutralise 1 g of sample with NaOH, add 30 ml of 20%  $\text{NH}_4\text{Cl}$  soln. to prevent pptn. of I and dilute to 50 ml. Add the reagents as before but allow to stand for 3 hr. before adding aq.  $\text{NH}_3$ . The same amount of pure  $\text{H}_2\text{SO}_4$  must be used to prepare calibration standards. Recoveries are 94 to 107%. *For organic matter*—Digest with  $\text{H}_2\text{SO}_4$ - $\text{HNO}_3$  in presence of HgO, separate Se as the bromide and reduce with  $\text{SO}_2$  and hydroxylamine. Dissolve the pptd. Se in HBr-Br soln. and remove excess of Br with phenol before adding the reagents. Recoveries are 96 to 101%.

P. D. FARR-RICHARD

**4237. Chemistry of selenium and selenium compounds. VI. Detection of small amounts of selenate with p-ethoxychrysoidine.** L. Barcza and E. Schulek (Inst. for Inorg. and Anal. Chem., L. Eötvös Univ., Budapest). *Mikrochim. Acta*, 1960,

(2), 261-266 (in German).—The sample soln. is concentrated to 0.5 ml and 0.05 g of KBr is added, followed by 0.5 ml of  $\text{H}_2\text{SO}_4$  (1:1) and 1 drop of ethanolic p-ethoxychrysoidine soln., and the mixture is heated on a boiling-water bath. The time taken for the colour to change from red to yellow is a measure of the  $\text{SeO}_4^{2-}$  present. Suitable concn. of reagent soln. are 0.01% for 5 to 50  $\mu\text{g}$  of  $\text{SeO}_4^{2-}$ , 0.004% for 1 to 5  $\mu\text{g}$ , and 0.001% for 0.2 to 1  $\mu\text{g}$ . Ferric iron,  $\text{Cu}^{2+}$ ,  $\text{NO}_3^-$  and  $\text{I}^-$  interfere seriously;  $\text{SeO}_3^{2-}$ ,  $\text{WO}_4^{2-}$ ,  $\text{Ni}^{2+}$  and  $\text{Hg}^{2+}$  interfere to a lesser degree.

H. M.

**4238. Determination of traces of selenium in tellurium.** C. R. Veale (D.S.I.R., Nat. Chem. Lab., Teddington, Middx., England). *Analyst*, 1960, **85**, 130-133.—For the calibration graph, aliquots of a standard soln. of  $\text{Se}^{4+}$  (prep. described) are treated with citric acid and the pH is adjusted to 2.7 to 2.9 with dil. aq.  $\text{NH}_3$ . 3:3'-Diaminobenzidine dihydrochloride is added and after 1 hr. the pH is adjusted to 8 to 8.2 with dil. aq.  $\text{NH}_3$ , the liquid is extracted with toluene, and the extinction of the extract is measured at 420 m $\mu$ . For Se contents  $> 7$  p.p.m., the soln. of the finely divided tellurium sample in dil.  $\text{HNO}_3$  is evaporated, the residue is dissolved in N NaOH, citric acid soln. is added and the procedure is then as for the calibration graph. Samples containing 0.5 to 10 p.p.m. are fumed with dil.  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$ , and the residue is dissolved in 6 N NaOH, a specified excess of conc. HCl and hydrazine dihydrochloride is added, and the liquid is heated to b.p. and set aside for 3 hr. at 40° to 60°. The supernatant liquid is removed, and the ppt. is washed by means of an immersion filter, then dissolved in dil.  $\text{HNO}_3$  and the soln. is evaporated; the residue is dissolved in dil. NaOH soln. and the Se is determined as before.

A. O. JONES

**4239. Separation and determination of traces of quadri- and sexa-valent selenium in telluric acid.** C. R. Veale (D.S.I.R., Nat. Chem. Lab., Teddington, Middx., England). *Analyst*, 1960, **85**, 133-139.—To the telluric acid in aq. soln. is added hydrazine dihydrochloride and the liquid is heated to b.p. and then set aside at 40° to 60° for 3 hr. The supernatant liquid is removed, the ppt. is washed by means of an immersion filter and then dissolved in conc.  $\text{HNO}_3$ , and the  $\text{Se}^{IV}$  is determined (*Anal. Abstr.*, 1960, **7**, 4238) as described earlier. The vol. of the filtrate and washings is reduced, conc. HCl is added to give a concn. of 2.1 N, a saturated soln. of hydrazine dihydrochloride is added, the ppt. of Te formed is separated, and the  $\text{Se}^{4+}$  produced by reduction of  $\text{Se}^{6+}$  are determined. For wt. of  $\text{H}_2\text{TeO}_6 > 17$  g, an aq. soln. is adjusted to pH 2.6 with acetic acid and is passed through an Amberlite IRA-400 column, which is then eluted with NaCl soln. The eluate is heated with hydrazine dihydrochloride soln. and Se is determined in the ppt.

A. O. JONES

**4240. Separation of tellurium from platinum and non-ferrous metals by means of a cationite.** N. P. Strel'nikova and G. G. Lystsova. *Zavod. Lab.*, 1960, **26** (2), 142-144.—Separation of Te from Cu, Ni, Fe and Pb is attained by passing 100 to 150 ml of the soln., 0.12 N in HCl, through a column (2 cm  $\times$  25 cm) of KU-2 ( $\text{H}^+$  form) at the rate of 3 to 4 ml per min. All the elements are retained. Elution of Te is carried out by means of 10 to 12% aq.  $\text{NH}_3$  (200 ml is sufficient to remove 200 to 300 mg of Te). Complete recovery of the Cu, Ni, Fe and Pb is obtained by subsequent treatment of the cationite

with HCl (1:1). Separation of Te from the chloride complexes of the platinum metals is attained by passage of the soln., 0.1 N in HCl, through the cationite column, which adsorbs the Te but not the platinum metals. When ammoniacal soln. containing Te together with Cu, Ni, Pt and Pd are passed through the cationite, only Te is not adsorbed. Selenium is not adsorbed by the cationite from acid or ammoniacal soln.

G. S. SMITH

**4241. The use of potassium manganate in quantitative analysis. IV. Determination of chromium(III).** G. den Boef and A. Daalder (Lab. Anal. Chem., Univ. of Amsterdam, Holland). *Z. anal. Chem.*, 1960, **172** (5), 360-362 (in German).—In 1 to 3 M alkali soln., excess of  $K_2MnO_4$  quant. oxidises  $Cr^{III}$  to chromate; the excess of  $K_2MnO_4$  is determined potentiometrically with  $As^{III}$ . The accuracy for 8 to 10 mg of  $Cr^{III}$  is within  $\pm 0.2\%$ , and for 1 mg of  $Cr^{III}$  it is  $\pm 4\%$ . *Procedure*—Add the sample (25 ml) to an excess of  $K_2MnO_4$  in 1 to 3 M alkali soln. containing  $H_2TeO_4$  (100 mg). Set aside the soln. for 1 hr., then titrate within 15 min. with an alkaline soln. of  $As^{III}$ . Neglect any determinations in which  $MnO_2$  is pptd.

J. P. STERN

**4242. Spectrophotometric determination of molybdenum with 2:3:7-trihydroxy-9-methyl-6-fluorone.** A. K. Majumdar and C. P. Savariar (Jadavpur Univ., Calcutta, India). *Anal. Chim. Acta*, 1960, **22** (2), 158-162.—The rose-red complex shows maximum absorption at 510 m $\mu$  and obeys Beer's law for a Mo concn. of between 0.2 and 3.0 p.p.m., the optimum range being 0.8 to 3 p.p.m. when the percentage relative analysis error is 2.8. In solution the complex contains Mo and the reagent in the ratio of 1:1. The instability constant of the complex is  $\approx 2.09 \times 10^{-6}$ . The following ions do not interfere— $F^-$ ,  $Cl^-$ ,  $NO_3^-$ ,  $ClO_4^-$ ,  $SO_4^{2-}$ , phosphate, acetate, tartrate, citrate and oxalate, and  $Fe^{3+}$ ,  $U^{6+}$ ,  $Al^{3+}$ ,  $Na^+$  and  $NH_4^+$ . Zirconium, Ti,  $CrO_4^{2-}$  and  $WO_4^{2-}$  all interfere at the 2 p.p.m. level.

E. G. CUMMINS

**4243. Oxidimetric determination of tungsten after reduction with zinc.** R. Geyer and G. Henze (Inst. f. anal. Chem., Tech. Hochschule für Chem., Leuna-Merseburg, Germany). *Z. anal. Chem.*, 1960, **172** (6), 409-413 (in German).—The influence on the reduction of  $W^{VI}$  of the amount and nature of the added zinc is discussed. Powdered zinc containing about 2% of Pb gives the best results. *Procedure*—Evaporate a soln., containing 50 to 250 mg of  $W^{VI}$ , to a small vol., add a 7-fold vol. of conc. HCl and reduce with 5 to 7 g of zinc powder, together with a little Pb acetate. Keep the soln. cooled to  $\pm 20^\circ$ . Pour the green soln. of  $W^{III}$  through cadmium turnings in a 10-cm column, the tip of which dips into a mixture of 50 ml of 0.1 M  $Fe_2(SO_4)_3$  and 10 ml of conc.  $H_3PO_4$ , and wash through with 100 ml of HCl (1:1). Titrate with 0.1 M  $Ce(SO_4)_3$  with ferrous-phenanthroline complex as indicator; a blank should also be performed. The standard deviation is  $\pm 0.321$  mg of  $WO_3$  (24 determinations of amounts from 52 to 173 mg).

P. D. PARR-RICHARD

**4244. Determination of uranium(VI) by reduction to uranium(III) in a Jones reductor.** J. H. Kennedy (Explosives Dept., E. I. du Pont de Nemours & Co., Inc., Wilmington, Del.). *Anal. Chem.*, 1960, **32** (2), 150-152.—Sexavalent U in soln. can be reduced quant. to  $U^{III}$  in a Jones reductor at concn.  $< 0.01$  M in M HCl or M  $HClO_4$ . The percolate

from the reductor is led directly into  $(NH_4)_2SO_4$ - $Fe_2(SO_4)_3$  soln. de-aerated with N. The  $Fe^{2+}$  formed are titrated within 1 hr. with  $K_2Cr_2O_7$  soln. No further de-aeration is then necessary. Phosphoric acid and Na diphenylaminesulphonate are used in the titration. The concn. of  $SO_4^{2-}$  must be  $< 0.01$  M, otherwise the yields are low. Other  $U^{IV}$ -complexing agents interfere; acetate does not. Titanium and Mo are also quant. determined.

R. M. S. HALL

**4245. Adsorption of uranium from a hydrochloric acid-ethanol solution on the strongly basic anion-exchange resin Dowex 1. Determination of microgram amounts of uranium in solid materials.** J. Korkisch, P. Antal and F. Hecht (Lehrkanzel für anal. Chem., II Chem. Inst., Univ. Vienna). *Z. anal. Chem.*, 1960, **172** (6), 401-408 (in German).—The separation of U from a 500-fold excess of  $Mo^{VI}$  or  $W^{VI}$  is described; large amounts of chlorides must be absent. After evaporation of a 1-g sample with HF, HF and  $HNO_3$  and finally with conc. HCl, the residue is dissolved in 4 N HCl, filtered and washed with 4 N HCl to make 100 ml. Ascorbic acid is added to a 25-ml aliquot to reduce  $Fe^{III}$  and finally 100 ml of ethanol and a further 0.5 g of ascorbic acid are added. After passing the soln. slowly through Dowex-1 resin (break-through capacity 18.5 mg of U per g), the resin is washed free from Fe with 2% ascorbic acid soln. and finally with 4 N HCl-ethanol (1:4). Uranium is then eluted with 0.1 N HCl saturated with ethyl ether, and determined polarographically. Analyses of coal ash, phosphates, bauxites and rocks containing W are given.

P. D. PARR-RICHARD

**4246. Spectrophotometric studies of organo-metallic complexes used in analytical chemistry. VI. Determination of uranium with quercetin-6-sulphonic acid.** Takuji Kanno (Res. Inst. of Mineral Dressing and Metallurgy, Tohoku Univ., Nagamachi, Sendai). *Japan Analyst*, 1959, **8** (10), 633-638.—Quercetin-6-sulphonic acid (I) forms a brown water-sol. complex with  $UO_2^{2+}$  in neutral soln., which gives an absorption max. at 460 m $\mu$ . The extinction is proportional to the concn. of U (1 to 12  $\mu$ g per ml) at pH 6.0 to 6.5 in the presence of  $> 2.4 \times 10^{-4}$  M I. With increase in concn. of  $NH_4^+$ , the extinction at  $< 465$  m $\mu$  decreases, whereas that at  $> 465$  m $\mu$  increases. When U is extracted with tributyl phosphate (II) from N  $HNO_3$  containing 30% of  $NH_4NO_3$ , there is no interference from ions other than Th, which is masked with EDTA (0.005%); U is also separated from other ions, including Th, Fe, Mo, W, Sb, Zn, Ni, Co, Cu, Mn and Pb, by extraction with II-hexane (1:1).

K. SAITO

**4247. Determination of uranium by amperometric titration.** V. F. Eskevich and L. A. Komarova. *Zhur. Anal. Khim.*, 1960, **15** (1), 84-87.—A method is suggested for the amperometric titration of U (up to 1  $\mu$ g per litre) with ammonium vanadate soln. The sample is prepared by the dithionite-phosphate or chromium-phosphate method and the titration is carried out without the application of an external potential to the bismuth reference electrode. The accuracy of the method is within 3%.

A. BURWOOD-SMITH

**4248. Spectrographic determination of uranium in ores and residues after leaching, by using the sifter method in an a.c. arc.** J. Czakow, Z. Radwan and B. Strzyżewska (Dept. of Anal. Chem., Inst. of Nuclear

Res., Warsaw). *Chem. Anal., Warsaw*, 1959, **4** (5-6), 819-828.—This new and simple method is suitable for application to ores and leaching residues containing significant amounts of Si and other common elements. Vertical copper electrodes were used, the upper a sifter electrode and the lower a flat rod. The sample was mixed with graphite powder (1:3, or less if the ores contained carbon). As excitation source a Swietnicki a.c. arc was used in which the 30-W transformer was replaced by a 400-W one, so that the high-frequency spark was more intense and caused the powder to fall out from the electrode. The analytical line U 4090.14 was compared with the internal standard line Mo 4083.03. The effect of various amounts of Mo on the excitation of the analytical line was investigated. The excitation was performed in an Ar-O atmosphere. A large glass spectrograph (ISP-51) was used. The method is suitable for U concn. from  $10^{-2}$  to  $10^{-1}$  %. The precision was  $\pm 2.8$  % and the coeff. of variation for a single measurement was  $\pm 4.7$  %. The apparatus is illustrated.

L. SMAKOWSKI

4249. Separation of uranium by reversed-phase partition chromatography. A. G. Hamlin and B. J. Roberts [U.K.A.E.E. (P.G.), Chem. Serv. Dept., Capenhurst Works, nr. Chester, England]. *Nature*, 1960, **185**, 527-528.—The method described effectively separates U from 10 times its weight of Cr, Cu, Al, Ni, V, Ca, Fe, Mo, W, Na, K, F<sup>-</sup>, PO<sub>4</sub><sup>3-</sup>, SO<sub>4</sub><sup>2-</sup> and Cl<sup>-</sup> and concentrated soln. of citric acid. The recovery with a 5-mg sample of U is 99%. Purified tributyl phosphate is used as the stationary phase, and low-density Kel F-300 moulding powder (100 to 200 mesh) as the solid support; 3 g of each are mixed and loaded as a slurry in 5.5 N HNO<sub>3</sub> into a tube of 7 mm internal diam. This column is washed with 5.5 N HNO<sub>3</sub>, and the sample (5 to 10 ml) containing < 50 mg of U in 5.5 N HNO<sub>3</sub> is poured in. The U is retained as a yellow band at the top of the column. The impurities are eluted with 5.5 N HNO<sub>3</sub> (3 × 10 ml) (1 to 2 ml per min.), and the U is eluted with 35 ml of H<sub>2</sub>O at the same rate. Thorium, Pu<sup>IV</sup> and Ce<sup>IV</sup> are retained on the column after the washing with HNO<sub>3</sub>, but Ce can be separated after reduction by SO<sub>2</sub> to Ce<sup>III</sup>. The column can be re-activated by being washed with 20 ml of 5.5 N HNO<sub>3</sub>.

S. BAAER

4250. Separation of uranium from accompanying metals by ion-exchange chromatography. D. I. Ryabchikov, P. N. Palei and Z. K. Mikhailova (V. I. Vernadsky Inst. of Geochem. and Anal. Chem., Acad. Sci., USSR, Moscow). *Zhur. Anal. Khim.*, 1960, **15** (1), 88-95.—The method is based on the behaviour of U and other elements with EDTA. Separation is possible in acid media in which U is present as a cation; most of the accompanying elements form an anion complex with EDTA and are not adsorbed by the cationite. Separation is also possible in almost neutral media in which the U is present as an unstable anion complex, and can be adsorbed on a carboxylic resin after decomposition of this complex. For materials rich in U, the cationite KU-2 (Na<sup>+</sup> form) was used to separate U from soln. at pH 1.7 to 1.9. Separation of U from soln. at pH 5 to 8 on Amberlite IRC-50 cationite (Na<sup>+</sup> form) can be used for ores that are either rich or poor in U, as well as for uranium soln.

A. BURWOOD-SMITH

4251. Cation-exchange behaviour of uranium(VI) on Amberlite IR-120: separation from mixtures. Shripad M. Khopkar and Anil K. De (Jadavpur

Univ., Calcutta, India). *Anal. Chim. Acta*, 1960, **22** (2), 153-158.—The efficiency of HCl (1, 2, 3 and 4 N), HNO<sub>3</sub> (1, 2 and 4 M), H<sub>2</sub>SO<sub>4</sub> (1 and 2 M), HClO<sub>4</sub> (2 M), acetic acid (2 N) and citric acid (2% and 5%) as eluents is discussed in terms of their elution constants. Uranium has been separated from Th, Zr, Ce<sup>III</sup>, Hg, Cu, Ni and phosphate.

E. G. CUMMINS

4252. Separation of uranium from titanium with cation-exchange resin. Koichi Tonosaki and Makoto Otomo (Fac. of Liberal Arts, Hiroaki Univ., Aomori-ken). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1959, **80** (11), 1290-1292.—Whilst ion-exchange separation of U<sup>VI</sup> (< 1 mg) from Ti (< 100 mg) is unsuccessful, that of U<sup>IV</sup> from Ti is satisfactorily effected with 2 N HCl as eluent. A 2 N HCl soln. containing Ti and U is treated with zinc amalgam and passed through a column (diameter, 1 cm; length 24 cm) of Amberlite IR-120(H) (60 to 100 mesh), and the column is washed with 2 N HCl (250 ml) at a rate of 2 ml per min.; U is retained on the column, and Ti passes through. The U is eluted with 2 N H<sub>2</sub>SO<sub>4</sub>. There is no interference from metal ions other than those of rare-earth and alkaline-earth elements and Th.

K. SAITO

4253. Simultaneous spectrophotometric determination of uranium and iron with acetylacetone. Masayoshi Ishibashi, Tsunenobu Shigematsu and Masayuki Tabushi (Chem. Dept., Fac. of Sci., Kyoto Univ., Sakyo-ku, Kyoto). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1959, **80** (9), 1018-1021.—The acetylacetone complexes of U (0.05 to 1 mg) and Fe<sup>III</sup> (0.02 to 0.15 mg) are extractable from an aq. soln. of pH 7.0 to 7.5 with butyl acetate, and exhibit absorption peaks at 365 and 440 mμ, respectively. The extinction is little affected by the amount of acetylacetone (I) and the working curve is linear for < 0.2 mg of Fe and < 1.2 mg of U. The extraction of U by CHCl<sub>3</sub> from an aq. soln. (40 ml) of pH ≈ 4 containing a small amount of I (5% aq. soln.) (2 ml) is negligible, whereas Fe (< 10 mg) passes into the CHCl<sub>3</sub> layer. The U in the aq. phase is then extracted from the neutralised soln. with butyl acetate and both metals are determined photometrically.

K. SAITO

4254. Spectrographic determination of aluminium in uranium. E. A. Vernyi and V. N. Egorov. *Zhur. Anal. Khim.*, 1960, **15** (1), 24-26.—The method is based on fractional distillation with a carrier. It was found that by mixing 3% or more of carbon powder with the sample the Al lines 3082.16 Å and 3092.71 Å were considerably strengthened, whilst the spectrum for U was not. Barium, as BaCO<sub>3</sub>, considerably decreased the influence of third elements on the spectra. By using carbon and BaCO<sub>3</sub>, the following did not interfere—CaF<sub>2</sub> (at concn. up to 3%), Fe (3%), Na (3%) and Mo (7%). Errors on samples of uranium containing  $1 \times 10^{-3}$  to  $3 \times 10^{-2}$  % of Al were 9 to 11%.

A. BURWOOD-SMITH

4255. Analytical application of the hanging mercury drop electrode. IV. Analysis of traces of impurities in uranium salts. W. Kemula, E. Rakowska and Z. Kublik (Inst. Phys. Chem., Acad. Sci., Univ. Warsaw, Poland). *J. Electroanal. Chem.*, 1960, **1** (3), 205-217 (in English).—The method described previously (*cf. Anal. Abstr.*, 1958, **5**, 3231) has been applied to the determination of < 0.01 p.p.m. of Cd and < 0.1 p.p.m. of Cu and Pb



in uranium salts. The supporting electrolyte is 0.1 M  $K_2CO_3$  and pptn. of carbonates limits the upper concn. of Cu to  $10^{-4}$  M and of Cd and Pb to  $10^{-5}$  M. The  $UO_2(CO_3)_2^{4-}$  complex is reduced at a more negative potential and does not interfere. The precision is  $\pm 10\%$ . A complete analysis takes 1 to 2 hr.

A. R. ROGERS

**4256. Absorptiometric determination of plutonium in the feed solution to the primary separation plant.** U.K.A.E.A. (Industrial Group, Operations Branch, Windscale). Report IGO-AM/W-115, 1960. 7 pp.—The Pu is converted into the quadrivalent state and extracted into a benzene soln. of benzethonium chloride. A soln. of thoron in the same solvent is added to the washed extract and the extinction of the soln. is measured in a Spekker absorptiometer with Ilford 503 and 605 filters.

N. E.

**4257. Determination of the fluoride ion by the use of the polarogram of cadmium.** Akio Iwase (Fac. of Liberal Arts, Yamagata Univ., Koshirakawa-cho). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1959, **80** (10), 1138-1141.—The replacement of Cd in the Cd-EDTA complex by  $Zr^{4+}$  is affected by the presence of  $F^-$  and the amount of  $Cd^{2+}$  liberated decreases linearly with increase in concn. of  $F^-$  (10 to 140 p.p.m.) under given conditions. The rate of the substitution is increased in the presence of  $NH_4SCN$  and equilibrium is reached within 40 min. in  $M NH_4SCN$  soln. The sample soln. is mixed with  $Zr(NO_3)_4$ ,  $NH_4SCN$ , Cd-EDTA and gelatin soln. to produce, respectively, 0.45 mM, 1 M, 2 mM and 0.01% soln., which are buffered with Na acetate to pH 4.7 to 5.0. The polarogram is recorded after 40 min. and the height of the wave due to  $Cd^{2+}$  is measured. Phosphate, sulphate ( $> 3$  mg per ml) and heavy-metal ions interfere.

K. SAITO

**4258. Direct-reading spectrochemical determination of fluorine in alumina.** P. E. Lemieux and R. H. Black (Aluminium Laboratories, Ltd., Arvida, Quebec, Canada). *Anal. Chem.*, 1960, **32** (2), 246-248.—Of various mixtures tested, a 1:1:1 mixture of sample,  $SrCO_3$  and graphite (total weight 600 mg) is best; excitation in air, with 6 amp. d.c., an exposure of 20 to 25 sec., and Al 2568 Å as internal standard are used. The SrF band is recorded at 5782 Å. The calibration is linear with a Quantometer and not quite linear with a Hilger medium quartz spectrograph up to 0.5% of F. The coeff. of variation (day-to-day reproducibility) is  $\pm 0.004\%$  in the range 0.0 to 0.1% of F and  $\pm 0.01\%$  in the range 0.0 to 0.5%. The corresponding standard deviations for chemical values are  $\pm 0.016$  and  $\pm 0.02$ .

R. M. S. HALL

**4259. Rapid determination of fluoride in silica-alumina catalyst by steam hydrolysis.** L. W. Gamble, W. E. Price and W. H. Jones (Res. Lab., Louisiana Div., Esso Standard Oil Co., Baton Rouge, U.S.A.). *Anal. Chem.*, 1960, **32** (2), 189-192.—Fluorine in siliceous materials is determined in silica apparatus by a modification of the method of Warf *et al.* (*Anal. Abstr.*, 1955, **2**, 2413). The qual. composition of the sample should be known. The sample is hydrolysed by steam in a silica tube at 760°, the exit steam being condensed and collected in borosilicate beakers. The condensate is kept alkaline with aq. NaOH soln. The  $F^-$  are determined by titration with 0.05 N thorium nitrate, with Na alizarinsulphonate as indicator. The residual F in the sample is about 0.05% after steaming; samples should contain more than 0.5%

of F. Free phosphoric acid in the sample interferes. For silica-alumina samples the mean result for three determinations in each of four laboratories for a synthetic material containing 0.506% of F was 0.498% with a standard deviation of  $\pm 0.016$ . For silica-alumina catalysts, which accelerate the fluoride hydrolysis, the method takes less than 1 hr.

R. M. S. HALL

**4260. Estimation of hydrogen fluoride in mixed-gas systems by infra-red spectroscopy.** A. M. Deane (Chem. Div., A.E.R.E., Harwell, England). A.E.R.E. Report AERE-R 3261, 1960. 30 pp.—Full details are given of experiments in which the effect of various gases on the absorption by HF at  $2.5 \mu$  was measured. The systems studied, at 20° and 60°, were HF, HF-N, HF-Ar, HF-N-Ar, HF-H<sub>2</sub>O-N, HF-UF<sub>6</sub> and HF-UF<sub>6</sub>-N. The broadening efficiencies of N, Ar and UF<sub>6</sub> were determined.

G. J. HUNTER

**4261. Determination of iodine in thallium(I) iodide precipitates.** E. Jeung and E. H. Huffman (Lawrence Radiation Lab., Univ. Calif., Berkeley). *Anal. Chem.*, 1960, **32** (2), 152-153.—Univalent Tl and I- are quant. oxidised by Br at pH 5. Trivalent Tl is not reduced by formic acid in the Kainrath oxidation of I- to  $IO_3^-$  (*Z. anal. Chem.*, 1942, **125**, 1), and subsequently liberates iodine, as do the  $IO_3^-$ , from KI. The iodine is then titrated with thio-sulphate. Starch is used and the end-point is the production of a soln. containing a yellow ppt. of thallium iodide. One hour is sufficient for the oxidation if no organic covering film has been used, otherwise up to 16 hr. is necessary. Errors range from -0.3% to +0.5%.

R. M. S. HALL

**4262. Potentiometric determination of manganese in ferromanganese and other manganese-containing material.** A. Jelinek and J. Hošala (Kovohuty Istebné, Czechoslovakia). *Hutn. Listy*, 1960, **15** (2), 137.—The Lingane-Karplus method can be used with excellent results for the analysis of various sorts of Mn-containing material. *Procedure*—Dissolve the sample (0.5 g) in conc.  $HNO_3$  (20 ml) and dilute to 500 ml. To 100 ml of this soln. add urea (0.5 g) and  $Na_2P_2O_7$  soln. (10%) (250 ml), adjust the pH to 6 to 7 and titrate with  $KMnO_4$  soln. (2.2 g per litre) potentiometrically with a platinum electrode vs. the S.C.E. The presence of Co, Cr, Fe, Ni, Cu, Mo, W and U causes no interference; V must be absent.

J. ZÝKA

**4263. Polarographic determination of manganese in glasses.** M. S. Zakharov, A. G. Stromberg and G. G. Rodnova (Tomsk Polytech. Inst.). *Zavod. Lab.*, 1960, **26** (2), 153-154.—The finely divided sample (0.1 g) is heated with 25 g of  $NH_4F$ , added in two or three portions, until gaseous products are removed. The residue is mixed with 2 g of oxalic acid, then evaporated to dryness and ignited at a red heat. The oxides that are formed are treated with 2 ml of conc. HCl and 10 ml of  $M Na_2SO_4$  (to retain Mn in soln.) and then neutralised to alizarin with aq.  $NH_3$ . After the addition of 40 ml of a soln. 0.1 M in aq.  $NH_3$ , 0.25 M in  $NH_4Cl$  and 0.25 M in  $Na_2SO_4$  and containing 0.025% of gelatin, the soln. is diluted to 100 ml and the polarogram for Mn is recorded.

G. S. SMITH

**4264. Radiochemical analyses through polarographic methods. II. Rapid procedure for technetium and ruthenium radionuclides in fission products.** D. L. Love and A. E. Greendale (Naval

Radiological Defense Lab., San Francisco). U.S. Atomic Energy Comm., Rep. USNRDL-TR-388, Nov., 1959. 27 pp.—An electrochemical determination for  $^{99m}\text{Tc}$  in fission-product mixtures was developed. The precision and accuracy of the method are better than those of the usual radiochemical methods and  $\approx 50$  analyses may be made in one day. The number of fissions and the amount of  $^{90}\text{Mo}$  are determined from the amount of  $^{99m}\text{Tc}$  found in the fission-product mixture.

NUCL. SCI. ABSTR.

**4265. Colorimetric determination of rhenium in the presence of molybdenum.** V. M. Tarayan and L. G. Mushegyan. *Izv. Akad. Nauk ArmSSR, Khim. Nauk.*, 1958, **11** (6), 397-408; Ref. Zhur., *Khim.*, 1959, (24), Abstr. No. 86,142.—The light absorption of the thiocyanate complexes of Re and Mo is studied as a function of wavelength and HCl concn. It is shown that to decrease the influence of Mo on the determination of Re it is best to measure the extinction in 5 N HCl at 428 m $\mu$ . The stability of the colour of the thiocyanate complexes of Re and Mo at high acidity is studied. As distinct from the thiocyanate complex of Mo, which under these conditions rapidly becomes decolorised, the thiocyanate complex of Re shows a constant optical density. The decolorisation of the thiocyanate complex of Mo is studied as a function of the Mo concn. It is established that Re can be determined in the presence of Mo in 5 N HCl if the amount of Mo is  $\geq 100 \mu\text{g}$  in 25 ml. The absorption spectra of the thiocyanate complex of Re are obtained in aq. soln., butanol or ethyl ether and in the presence of  $\text{Fe}^{3+}$ . It is shown that in  $\text{H}_2\text{SO}_4$  soln. in the presence of Re, Mo is selectively reduced by mercurous nitrate if the  $\text{H}_2\text{SO}_4$  concn. is  $\geq 5 \text{ N}$ ; Re is reduced by mercurous nitrate in a medium  $> 5 \text{ N}$  in  $\text{H}_2\text{SO}_4$ . Milligram amounts of Mo can be easily separated from microgram amounts of Re.

C. D. KOPKIN

**4266. Colorimetric micro-determination of iron.** M. Papařil and A. Kleinstein (Univ. "Al. I. Cuza", Iași). *An. Științ. Univ. "Al. I. Cuza" din Iași*, 1959, **5** (1), 141-147 (in French).—The colour given with *o*-phenylenediamine (I) by  $\text{Fe}^{3+}$  is yellow in concn. of 0.01  $\mu\text{g}$  per ml, but orange at concn. of 1.7  $\mu\text{g}$  per ml, and dark red at concn. of  $> 15 \mu\text{g}$  per ml. The reagent, a 0.1 M ethanolic soln. of I acidified with conc. HCl, remains stable for 24 hr. The pH for max. intensity should be between 1 and 2. Although a blue filter gives max. absorption, the Beer-Lambert law is not followed at low concn., and for this reason a green filter is used. The standard curve shows two straight portions, intersecting at a concn. of 0.76  $\mu\text{g}$  of Fe per ml. The metals Na, K, Ca, Mg, Al, Zn, Cd, Cu, Hg, Mn, Co, Ni, Pb and Cr do not interfere even at concn. 50 to 60 times that of the Fe. The method is particularly suitable, therefore, for biological liquids.

H. SHER

**4267. Volumetric determination of small amounts of iron.** V. P. Hirsjärvi, B. Salovius and M. Uosukainen (State Agric. Chem. Lab., Helsinki, Finland). *Mikrochim. Acta*, 1960, (2), 220-230 (in German).—Small amounts of  $\text{Fe}^{II}$ ,  $\approx 1 \text{ mg}$  in soln. containing  $\text{H}_2\text{SO}_4$  and  $\text{H}_3\text{PO}_4$ , can be titrated with  $\text{K}_2\text{Cr}_2\text{O}_7$  soln. When diphenylamine-*p*-sulphonic acid (I) is used as indicator the  $\text{H}_2\text{SO}_4$  concn. should be between 0.25 N and 3.0 N, preferably 1.5 N, and the  $\text{H}_3\text{PO}_4$  concn. should be not greater than 0.1 N. Amounts of Cu, Co and Mn equal to

that of the  $\text{Fe}^{II}$  can be tolerated, also 80 mg of Ca. When N-phenylanthranilic acid is used, the soln. should be 2.0 N with respect to  $\text{H}_2\text{SO}_4$  and 0.25 N with respect to  $\text{H}_3\text{PO}_4$ . Cobalt (1 mg) does not interfere, but the same amounts of Cu and Mn give high results. 1:10-Phenanthroline hydrochloride may be used under the same conditions, and amounts of Cu, Co and Mn equal to that of the  $\text{Fe}^{II}$  do not then interfere. Only Mn interferes when 2:2'-dipyridyl is used. I is thus to be preferred, especially since  $\text{Fe}^{III}$  can be titrated after reduction with Cd.

H. M.

**4268. Analytical aspects of some organic acids. IV. Direct complexometric titration of iron(III) with EDTA, with 3-hydroxy-2-naphthoic acid as indicator.** C. S. Pande and T. S. Srivastava (Chem. Dept., Lucknow Univ., India). *Z. anal. Chem.*, 1960, **172** (5), 356-359 (in English).—The rapid determination of  $\text{Fe}^{III}$  with EDTA at 30° to 35° and at pH 2.2 to 4.4 is possible by the use of K 3-hydroxy-2-naphthoate (I) as indicator. The blue complex of I with  $\text{Fe}^{III}$  is less stable than the yellow EDTA- $\text{Fe}^{III}$  complex, and the colour changes very sharply at the end-point. The accuracy for 23 to 116 mg of  $\text{Fe}^{III}$  is within  $\pm 0.3\%$ . Beryllium,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{UO}_2^{2+}$  and  $\text{Mn}^{2+}$  do not interfere, but  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{ZrO}^{2+}$ ,  $\text{VO}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Ti}^{4+}$ ,  $\text{Ce}^{4+}$  and  $\text{Th}^{4+}$  interfere.

J. P. STERN

**4269. Determination of iron and iron-aluminium mixtures by titration with EDTA.** D. G. Davis and W. R. Jacobsen (School of Chem., Georgia Inst. of Technol., Atlanta, Ga., U.S.A.). *Anal. Chem.*, 1960, **32** (2), 215-217.—At pH 1, Al does not interfere with the spectrophotometric titration of Fe with EDTA, with 5-sulphosalicylic acid as indicator. Aq. EDTA (disodium salt) soln. is used and standardised against Bi at pH 1.2 to 1.4. The disappearance of the Fe-sulphosalicylic acid complex is followed at 510 m $\mu$ . Visual titration is very difficult. Aluminium does not interfere when present in amount  $>$  twice that of Fe when the concn. of Fe is  $<$  0.01 M. The accuracy is then within 0.3%.

R. M. S. HALL

**4270. Spectrographic analysis of ferro-alloys. II. Determination of lead, copper and zinc in ferromanganese.** Yu Yokoyama (Inst. for Iron, Steel and Other Metals, Tohoku Univ., Katahira-cho, Sendai). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1959, **80** (12), 1423-1426.—Conditions for the determination of Pb, Cu and Zn ( $<$  0.1%) in ferromanganese with the aid of an interrupted arc method were examined. The intensity of the emission lines decreases with length of exposure and exhibits a max. when the sample powder is mixed with the same wt. of carbon. The optimum conditions are as follows—distance between the carbon electrodes, 2.5 mm; diameter of electrodes, 5 mm; sample-hole, diameter, 2.5 mm, depth, 3 mm; current, 10 amp.; terminal voltage, 200 V; interruption factor 1/3; period, 1/6 sec.; exposure, 25 sec.; line-pairs, Mn 2830-79 - Pb 2833-07, Mn 3296-88 - Cu 3272-96, Mn 3296-88 - Zn 3302-59, and Mn 3296-88 - Fe 3286-76 Å. The content of Fe has little influence on the analysis.

K. SAITO

**4271. New volumetric method for determination of potassium ferrocyanide with *o*-dianisidine as an adsorption indicator.** H. Basińska and K. Przybyszewska (Dept. of Inorg. Chem., Copernicus Univ., Toruń). *Chem. Anal., Warsaw*, 1959, **4** (5-6), 783-790.—The method is based on the



direct titration of standard  $\text{AgNO}_3$  soln. with  $\text{K}_4\text{Fe}(\text{CN})_6$  soln. To 300-ml flasks were added 5, 10, 15 or 20 ml of 0.05 or 0.1  $M$   $\text{AgNO}_3$  and 3 to 5 drops of  $\alpha$ -dianisidine indicator (0.1 g dissolved in 25 ml of 2.5%  $\text{H}_2\text{SO}_4$  soln. and made up to 100 ml with  $\text{H}_2\text{O}$ ) and the soln. were titrated with 0.1 or 0.05  $M$   $\text{K}_4\text{Fe}(\text{CN})_6$ . The colour change of the ppt. (pink to blue) at the end-point is related to adsorption phenomena on the surface of the colloidal particles of  $\text{Ag}_4\text{Fe}(\text{CN})_6$ . The titration should be performed in neutral or acetic or nitric acid medium. The method is simple and accurate.

L. SMAKOWSKI

**4272. Determination of trace elements in cast iron.** R. C. Rooney (B.C.I.R.A., Birmingham). *J. Res. Brit. Cast Iron Ass.*, 1960, **8** (2), 193-199.—The unreliability of the methods in use for determining traces of various elements in cast iron is discussed. A list of the requirements and the criteria to be satisfied is given. Some successful techniques obtained from a study of the methods used to prepare carrier-free radioactive isotopes are described and examples of procedure at B.C.I.R.A. for separation of Sb, Pb and Bi, Al, Co, Zn, B and Cr are given. C. H. COWPER-COLES

**4273. Spectrographic determination of traces of metal impurities in iron.** M. Kotrbová (Phys. Inst. Acad. Sci., Prague). *Hutn. Listy*, 1960, **15** (2), 131-132.—*Procedure*—Dissolve the sample (1 g) in  $\text{HCl}$  (20 ml), oxidise with several drops of  $\text{HNO}_3$ , remove nitrogen oxides by boiling and evaporate on the water bath to dryness. Add  $\text{HCl}$  (15 ml) and repeat the evaporation. Transfer into a 250-ml separating-funnel (A) with  $\text{HCl}$  (30 ml), add *iso*-butyl methyl ketone (I) (30 ml) and shake. Separate the lower layer and transfer into another separating-funnel (B). Wash the soln. in A with  $\text{HCl}$  (5 ml) and transfer the washings to B. Shake the acid in B with I (40 ml), run off the acid layer and wash the I with more acid. Evaporate the combined acid extracts to a small vol. and mix with powdered carbon (100 mg) moistened with  $\text{HNO}_3$  and evaporate under an i.r. lamp. Add a soln. of Bi (0.1 mg), evaporate to dryness, add  $\text{HCl}$  and repeat the evaporation. Carry out the spectrographic determination on the residue. The following relative errors were found: Ni, Cr, Pb,  $\pm 10\%$ , Mn  $\pm 15\%$ , Co  $\pm 17\%$ , Cu  $\pm 18\%$ . J. ŽYKA

**4274. Experience with direct-recording spectrographs in the steel-works laboratory.** IX. G. Wollweber and R. Fehle. *Arch. Eisenhüttenw.*, 1959, **30** (11), 655-657.

X. H. Hildebrand and W. Diehl. *Ibid.*, 1959, **30** (11), 659-660.

XI. T.-K. Willmer and W. Liedtke. *Ibid.*, 1959, **30** (12), 713-714.

XII. J. Bruch. *Ibid.*, 1959, **30** (12), 715-721. (For earlier sections see *Anal. Abstr.*, 1960, **7**, 1755.)

**4275. Spectrographic determination of residual elements in steel by the excitation index technique.** K. M. Bills (Mond Nickel Co. Ltd., Birmingham). *J. Iron St. Inst.*, 1960, **194** (2), 193-198.—The preliminary work by a Study Group of the B.I.S.R.A. Spectrographic Analysis Sub-Committee is described. A common basis for the use of a.c. and d.c. arc source units and an "excitation index" has been suggested for the determination of Co, Ni, Ti, Zr, Cu, Sn, Mo, Cr, Nb, V and Al down to 0.01% concn. A mean coefficient of variation of  $\pm 4.2\%$  has been achieved. J. W. O. PYEMONT

**4276. Determination of trace elements [in steel].** N. W. H. Addink (Res. Lab., M. V. Philips Gloeilampenfabrieken, Eindhoven). *J. Iron St. Inst.*, 1960, **194** (2), 199-211.—A short description of complete evaporation of the material through a d.c. carbon arc during spectrographic analysis is given. A short account of the determination of trace elements by a method involving all the elements being taken into solution as perchlorates and spectrochemically analysed is also given. Spectrochemical and X-ray fluorescence methods are compared. J. W. O. PYEMONT

**4277. Determination of micro quantities of boron in steel by a solvent-extraction method.** L. Pasztor, J. D. Bode and Q. Fernando (Graham Res. Lab., Jones & Laughlin Steel Corp., Pittsburgh, Pa.). *Anal. Chem.*, 1960, **32** (2), 277-281.—The steel (0.1 g) is dissolved in  $\text{H}_2\text{SO}_4$ - $\text{H}_3\text{PO}_4$ . For soluble B, the B in the soln. is converted into  $\text{BF}_4^-$ , the complex with methylene blue is extracted into 1:2-dichloroethane and the extinction at 660  $m\mu$  is measured against dichloroethane. The content of B is read from a calibration curve. For insoluble B, the residue from dissolution is fused with  $\text{Na}_2\text{CO}_3$  followed by the above procedure. Reagent blank determinations are necessary. For 0.2 to 25  $\mu\text{g}$  of B the standard deviation is  $\pm 0.1 \mu\text{g}$  (6 to 18 determinations). R. M. S. HALL

**4278. Determination of aluminium in precipitation-hardening stainless steel and high-temperature alloys.** L. A. Machlan, J. L. Hague and E. J. Meros (Nat. Bur. of Standards, Washington, D.C., U.S.A.). *J. Res. Nat. Bur. Stand., A*, 1960, **64** (2), 181-184.—The sample (2 g) is dissolved in warm dil. aqua regia (1:1), and Al is selectively pptd. with 8-hydroxyquinoline at pH 9.2 to 9.4 and  $\approx 90^\circ$  from an ammoniacal soln. containing citric acid (50%, w/v) and NaCN (to complex Cr, Co, Cu, Ni and Fe). The ppt. is collected, ignited slowly to  $\approx 700^\circ$  with the addition of solid oxalic acid, and the  $\text{SiO}_2$  in the ignited residue is removed with  $\text{H}_2\text{SO}_4$  plus HF. The oxides are then fused with  $\text{K}_2\text{S}_2\text{O}_8$ , the melt is dissolved in  $\text{HCl}$  (1:5), a small amount of iron soln. is added, and another pptn. is made with boiling 30% (w/v) aq. NaOH soln. to remove Mn, Ti, Zr, Mg and other elements. An aliquot of the cool filtrate (containing  $\text{HCl}$  and citric acid) is adjusted to a pH of  $\approx 9.3$  with aq.  $\text{NH}_3$ , NaCN is added, followed by  $\text{H}_2\text{O}_2$  (to complex residual Ti, Nb, V, Mo and other elements), and the final pptn. of Al is made at  $55^\circ$  to  $60^\circ$  with 8-hydroxyquinoline. The ppt. is collected on a glass frit, dried and weighed. The working range is 0.5 to 5% and the positive error is  $\leq 1\%$ ; six analyses can be completed in one day. W. J. BAKER

**4279. Determination of aluminium nitride in steel with methanolic bromine.** Yosaburo Okura (Res. Lab., Kamaishi Works, Fuji Iron and Steel Ind., Kamaishi). *Japan Analyst*, 1959, **8** (10), 646-655.—From a consideration of possible errors in the ester-halogen method of Beeghly (*Brit. Abstr. C*, 1950, 219; 1952, 537) it is concluded that methanolic Br (Werner, *Z. anal. Chem.*, 1941, **121**, 385) is a better solvent and that Al and N should be determined in both the residue and the filtrate. *Procedure*—Treat the sample (1 g) at room temp. for 2 hr. with methanol (50 to 100 ml) and Br (4 to 5 ml). Filter through a paper that has previously been treated successively with hot dil.  $\text{H}_2\text{SO}_4$ , water and methanol. *Residue*—After drying for 1 hr. at  $105^\circ$ , treat the paper and residue with

6 N H<sub>2</sub>SO<sub>4</sub> (10 ml) for 1 hr. Add N NaOH (150 ml) and tin (10 g), distil under reduced pressure and collect  $\approx$  100 ml of distillate in 0.1 N H<sub>2</sub>SO<sub>4</sub>. Determine NH<sub>4</sub><sup>+</sup> in the distillate by nesslerisation and photometry, and Al in the distillation residue photometrically by treatment with 8-hydroxyquinoline and extraction into benzene. *Filtrate*—Acidify with H<sub>2</sub>SO<sub>4</sub>, evaporate to dryness under reduced pressure, extract the residue with water, add N NaOH (150 ml) and distil, and determine NH<sub>4</sub><sup>+</sup> and Al as described above. The apparatus is illustrated. K. SAITO

**4280. Simultaneous determination of carbon and sulphur in steel.** C. E. A. Shanahan and R. H. Jenkins (R. T. B. Central Res. Lab., Aylesbury). *Metallurgia, Manch.*, 1960, **61**, 43-47.—A Ströhlein unit is used and the results obtained with standard steels show that this technique is reliable. Steel (1.0 g) is burnt in O at 1280° without pre-heating; the combustion time for the complete evolution of S decreases as the flow-rate of the exit O increases; the decrease falls off when the O flow attains  $\approx$  300 ml per min. The total vol. of exit gases necessary for complete evolution of S is  $\approx$  600 ml regardless of O flow-rate. Overall combustion time is increased with a 2-min. pre-heating but the total vol. of exit gases for complete evolution of S is reduced, e.g., with a flow-rate of 300 ml per min. only 475 ml of gas is necessary. S.C.I. ABSTR.

**4281. Micro-zonal carbide analysis on the surface of molybdenum steel fractures.** L. V. Zaslavskaya and N. M. Popova. *Zavod. Lab.*, 1960, **26** (2), 135-137.—The fractured test-piece is coated, apart from the fractured surface itself, with a soln. of perchlorinated vinyl resin, and subjected to electrolysis with a platinum wire as cathode for 5 min. at 25 mA in 25 ml of 0.01 N HCl. Material depositing on the cathode is dissolved in 5 drops of 20% HCl soln. and returned to the soln. which is then analysed for the alloying elements and also for Fe. The results refer to elements that had been present in solid soln. The washed and dried sample is treated at 50° to 60° for 45 min. with 2 ml of 30% H<sub>2</sub>O<sub>2</sub> soln. and 1 ml of ethanol, and the content of Mo is determined. The result corresponds to the amount of Mo that had been present as carbide.

G. S. SMITH

**4282. Application of a Dumas technique for the determination of traces of nitrogen in cast iron and steel.** J. Coulombeau and E. Jaudon. *Chim. Anal.*, 1960, **42** (2), 61-68.—The sample (1 g for an ordinary steel or cast iron, 0.3 g together with 0.6 g of N-free iron for steel with a high content of Cr, 0.5 g with 0.5 g of N-free iron for 18:8 or titanium steels, and 2 to 5 mg for nitrides) is mixed with 12 g of Pb(BO<sub>2</sub>)<sub>2</sub>. The furnace is run at 1050° and CO<sub>2</sub> is passed through the apparatus. The gases are freed from O with copper gauze, and CO is oxidised by CuO, Hopcalite and I<sub>2</sub>O<sub>5</sub>. The N is collected in a nitrometer over 50% KOH soln. The method is very sensitive, detecting as little as 0.0007% on a 1-g sample. The error for steel and cast iron is  $\approx$  0.0009%, for alloy steel  $\approx$  0.0018%, for chromium steel  $\approx$  0.0030% and for nitrides  $\approx$  0.45%. J. H. WATON

**4283. Chronopotentiometric determinations at solid electrodes. Determination of manganese in steels.** D. G. Davis and J. Ganchoff (Georgia Inst. of Technol., Atlanta, Ga.). *J. Electroanal. Chem.*, 1960, **1** (3), 248-255 (in English).—Dissolve the sample (1 g containing  $\approx$  10 mg

of Mn) in HNO<sub>3</sub> (1:3) (25 ml), boil, cool, dilute to 100 ml, add conc. H<sub>2</sub>SO<sub>4</sub> (14 ml) and potassium periodate (0.5 g), boil for 3 min., cool and dilute to 250 ml. Record the chronopotentiogram at a gold electrode with a known current (*i*), such that the transition time (*t*) measured at +0.80 V vs. the S.C.E. is in the range 28 to 32 sec. Treat similarly a standard alloy and calculate the concn. (*c*) of Mn by use of the equation—

$$\frac{c_1}{c_2} = \frac{i_1}{i_2} \sqrt{\frac{t_1}{t_2}}$$

The chronopotentiometric method is at least as accurate as the colorimetric method and is free from interference by Cr, Ni, Co and Fe.

A. R. ROGERS

**4284. Determination of cobalt by oxidation with potassium molybdicyanide.** B. Kratochvil and H. Diehl (Dept. of Chem., Iowa State Univ., Ames, U.S.A.). *Talanta*, 1960, **3** (4), 346-350 (in English).—Bivalent cobalt is determined with K<sub>2</sub>Mo(CN)<sub>8</sub> (I) either titrimetrically or coulometrically. The titrimetric method is a modification of the potentiometric ferricyanide method. An excess of I [freshly prepared by oxidation of K<sub>2</sub>Mo(CN)<sub>6</sub> (II) with PbO<sub>2</sub> and H<sub>2</sub>SO<sub>4</sub>] is added to the test soln. containing ammonium citrate and conc. aq. NH<sub>3</sub>, and the unchanged I is titrated with CoSO<sub>4</sub> soln. By this procedure the potential change at the end-point is 0.6 V. Tervalent Fe does not interfere; Fe<sup>3+</sup> must be first oxidised (peroxide). If fluoride instead of citrate is used, Mn can be determined with the Co; Fe will then interfere. The coulometric method obviates the preparation and standardisation of I. II is added to a citrate-aq. NH<sub>3</sub> soln. containing the Co<sup>2+</sup>. Platinum electrodes are used and the coulombs necessary to just raise the solution potential from the Co<sup>2+</sup>-Co<sup>3+</sup> system are determined. The accuracy (6 determinations of each amount) is within 1% with a spread of 1%. Iron and manganese interfere. R. M. S. HALL

**4285. Chemical analysis with organic reagents. VI. Colorimetric determination of cobalt with NN'-ethylenedi-(4-methoxy-1:2-benzoquinone-1-oxime-2-imine).** Michio Mashima (Fac. of Engng, Niigata Univ., Nagaoka, Niigata-ken). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1959, **80** (11), 1260-1263.—The reagent (I) was prepared by treating 5-methoxy-2-nitrosophenol (Imura and Torii, *Japan Analyst*, 1955, **4**, 177) with ethylenediamine in benzene. I is sol. in water and gives a characteristic coloration with Co (red), Cu (purple), Ni (brown) Hg (red), Fe<sup>III</sup> (black), Mn (green), Pb (orange), Pd (scarlet) and Fe<sup>II</sup> (blue). The Co-I complex is extractable with CHCl<sub>3</sub> from neutral or acid soln. and has an absorption max. at 381 mμ. The extinction is proportional to concn. for  $< 2 \mu\text{g}$  of Co per ml of CHCl<sub>3</sub>. The excess of I in CHCl<sub>3</sub> is back-extracted with 0.5 to 2 N aq. NH<sub>3</sub> soln.

**VII. Application of the colorimetric determination of cobalt with NN'-ethylenedi-(4-methoxy-1:2-benzoquinone-1-oxime-2-imine).** Michio Mashima. *Ibid.*, 1959, **80** (11), 1263-1265.—When the Co-I complex is extracted with CHCl<sub>3</sub> from an aq. soln. of pH 1 to 3.5 in the presence of EDTA, there is no interference from ions other than Fe and a large amount of NH<sub>4</sub><sup>+</sup>. Ferric iron oxidises I, and the Fe<sup>II</sup>-I complex is extractable with CHCl<sub>3</sub>. In the presence of Fe<sup>III</sup>, the CHCl<sub>3</sub> layer is shaken with 2 N aq. NH<sub>3</sub> soln. containing hydroxyammonium chloride to transfer the Fe<sup>II</sup> into the aq. phase.

The oxidised **I** in the  $\text{CHCl}_3$  is removed by shaking with 3  $N$   $\text{H}_2\text{SO}_4$ . This method can be satisfactorily applied to the analysis of geochemical samples.

**VIII. Colorimetric determination of ferrous iron with NN'-ethylenedi-(4-methoxy-1:2-benzoquinone-1-oxime-2-imine).** Michio Mashima. *Ibid.*, 1959, 80 (11), 1265-1267.—**I** reacts with  $\text{Fe}^{II}$  in acid (pH 1.3 to 8) soln. to give a green complex, which becomes blue in ammoniacal soln. (max. absorption at 685  $m\mu$ ). The working curve is linear for  $< 2.5$   $\mu\text{g}$  of  $\text{Fe}$  per ml. Copper, Ni and Co, which form coloured complexes with **I** in acid soln., are removed by shaking the acid soln. with  $\text{CHCl}_3$ . There is no interference from foreign ions other than phosphate.

**IX. Colorimetric determination of palladium with NN'-ethylenedi-(4-methoxy-1:2-benzoquinone-1-oxime-2-imine).** Michio Mashima. *Ibid.*, 1959, 80 (11), 1267-1269.—Palladium forms an orange ppt. with **I** in acid soln. and the complex is extracted with  $\text{CHCl}_3$  from the aq. layer of pH 1 to 3.5. When the excess of **I** is removed by shaking with 2  $N$  aq.  $\text{NH}_3$ , the extinction is proportional to the concn. of Pd for  $< 8$   $\mu\text{g}$  per ml of  $\text{CHCl}_3$ . There is no interference from Fe, Ni, Pb, Zn or Hg. The Pd-**I** complex in  $\text{CHCl}_3$  is decomposed by shaking with 1 to 3  $N$   $\text{H}_2\text{SO}_4$ , whereas the Co-**I** complex is not. The  $\text{H}_2\text{SO}_4$  layer containing the Pd is neutralised, the pH is adjusted, and the soln. is again treated with **I** and  $\text{CHCl}_3$  for colorimetric determination. K. SAITO

**4286. Photometric determination of cobalt.** A. V. Vasserberg. *Trudj Leningr. Khim.-Farmatsevt. Inst.*, 1959, (6), 13-22; *Ref. Zhur. Khim.*, 1959, (24), Abstr. No. 86,152.—Photometric methods for the determination of small amounts of Co, based on its dimethylglyoxime complex (0.05 to 5  $\mu\text{g}$  of  $\text{Co}^{2+}$  per ml) and its nitroso-R salt complex (0.125 to 2.5  $\mu\text{g}$  of  $\text{Co}^{2+}$  per ml) have been developed and tested. The sensitivity is  $\pm 0.01$  to  $\pm 0.02$   $\mu\text{g}$  of Co with dimethylglyoxime and  $\pm 0.01$   $\mu\text{g}$  of Co with nitroso-R salt. C. D. KOPKIN

**4287. Spectrophotometric determination of cobalt and nickel with oxamidoxime.** G. A. Pearce, jun., and R. T. Pflaum (Dept. of Chem., State Univ. of Iowa, Iowa City, U.S.A.). *Anal. Chem.*, 1960, 32 (2), 213-215.—The sample containing Co and Ni is dissolved, HCl is added and the soln. is passed through a Dowex 1-X8 ion-exchange column. On addition of oxamidoxime (diaminoglyoxime) as a 0.1  $M$  soln. and solid Na acetate to raise the pH to 8 to 9.5 the nickel is quant. pptd. The filtrate and washings are measured at 350  $m\mu$ . The Co content is read from a calibration curve. The nickel ppt. is dissolved and the extinction at 233  $m\mu$  measured. The Ni content is read from a calibration curve. Interference is given by  $\text{Fe}^{3+}$  and  $\text{Cu}^{2+}$ , but these are removed on the ion-exchange column;  $\text{V}^{5+}$  and  $\text{Pb}^{2+}$  interfere, as do  $\text{Ag}^+$ ,  $\text{Mn}^{2+}$ ,  $\text{Cr}^{3+}$  and  $\text{Al}^{3+}$  at moderate concn. The accuracy is quoted at  $\pm 2\%$ . R. M. S. HALL

**4288. Studies on retention analysis for the determination of substances separated by paper chromatography. I. Determination of nickel.** Shoichi Yamada (Fac. of Educ., Mie Univ., Tsu). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1959, 80 (12), 1441-1444.—Retention analysis (*cf.* Wieland, *Naturwissenschaften*, 1948, 35, 29) was applied to the determination of Ni (0.1 to 30  $\mu\text{g}$  per spot) separated paper-chromatographically with acetone and HCl (50:3). When dithio-oxamide (**I**) or dimethylglyoxime (**II**)

is used as locating agent, the area of the coloured spot is proportional to the amount of Ni. The working curve is prepared by the use of reagents of varied concn. and the lower and the upper limits of determination are 0.08 and 15  $\mu\text{g}$  with **I** and 1 to 30  $\mu\text{g}$  with **II**, respectively. The spots of Co and Fe are separated with the same developer.

**II. Determination of copper.** Shoichi Yamada. *Ibid.*, 1959, 80 (12), 1444-1447.—When Cu that has been separated chromatographically with a mixture of acetone, conc. HCl and water (10:1:1) is treated with **I**, the coloured area is proportional to the amount of Cu. Three linear working curves are obtained for 0.2 to 1, 1 to 7, and 7 to 40  $\mu\text{g}$  of Cu with 2, 5, and 30 mg of **I** in a mixture of butanol and water (6:1) (35 ml). Benzoin  $\alpha$ -oxime is also useful as colour reagent, but the sensitivity is less (2  $\mu\text{g}$ ). K. SAITO

**4289. The analytical chemistry of the pyridine thiocyanates. II. The separation of ruthenium and palladium.** J. H. W. Forsythe, R. J. Magee and C. L. Wilson (Chem. Dept., The Queen's Univ., Belfast, N. Ireland). *Talanta*, 1960, 3 (4), 324-329.—Palladium is extracted into isobutyl methyl ketone (**I**) as  $\text{PdPy}_2(\text{SCN})_2$  from alkaline (pH 11) soln. containing an excess of KSCN and a little pyridine. The extinction is measured at 345  $m\mu$  against **I** and the amount of Pd is read from a calibration curve. The remaining soln. containing the Ru, KSCN and some pyridine, is quickly adjusted to a 2  $N$  acid soln. by addition of conc. HCl, and heated, and the ruthenium-thiocyanate complex changes from red to blue. This blue complex is extracted into **I** and the extinction is measured at 570  $m\mu$  against **I**. The amount of Ru is read from a calibration curve. The two determinations do not mutually interfere although pptn. may occur if the pH adjustment is too slow. Typical accuracies are within 2% for amounts of 30 to 750  $\mu\text{g}$ .

**III. The separation of rhodium, palladium and platinum.** J. H. W. Forsythe, R. J. Magee and C. L. Wilson. *Ibid.*, 1960, 3 (4), 330-334 (in English).—Pyridine is added to a soln. of the ions at about pH 2.5 until the pH value reaches 6.0, then KSCN is added, and the soln. is extracted with **I** to remove the palladium complex. The remaining soln. is adjusted to pH 2.0 (aq. HCl) and heated to 90°, then cooled and extracted with **I** to remove the platinum complex. To the remaining soln. are added 4% aq. KSCN soln. in excess and conc. HCl until the acid concn is 3 to 4  $N$ , and the cold soln. is extracted with **I** to remove the rhodium complex. The extinctions of the palladium, platinum and rhodium complexes are measured, respectively, at 345, 385 and 380  $m\mu$ , with **I** as standard for the first two and **I** saturated with 2  $N$  HCl for the third, and the values are referred to calibration curves. The complete separation and determination takes about 90 min. Minimum amounts determinable are 25  $\mu\text{g}$  for Pd (with an error  $< 2\%$ ) and 50  $\mu\text{g}$  for Pt and Rh (with an error  $< 10\%$ ). R. M. S. HALL

**4290. Separation of rhodium from platinum with the aid of ion-exchange resins.** F. Coufalik and M. Svach (Moravian Chem. Works, Ostrava, Czechoslovakia). *Z. anal. Chem.*, 1960, 173 (2), 113-115 (in German).—Alloys of Pt and Rh are dissolved in  $\text{HNO}_3$ -HCl (1:3) and the soln. is adjusted to pH 3.5. The strongly basic Anionit OAL anion-exchange resin (Cl<sup>-</sup> form) then retains Pt as  $(\text{PtCl}_4)^{2-}$ , while Rh is eluted with 0.2  $M$  HCl. The Rh in the eluate is determined photometrically after reduction

to  $Rh^{3+}$  with  $SnCl_2$ . Finally, Pt may be eluted slowly with 2 M aq.  $NH_3$ . The average recovery of Rh (1.0 to 3.0 mg per 250 ml) is 96.5%.

J. P. STERN

**4291. Thiophen derivatives as analytical reagents. 2-Thiophen-trans-aldoxime, a new reagent for palladium.** S. G. Tandon and S. C. Bhattacharya (Nat. Chem. Lab., Poona, India). *Anal. Chem.*, 1960, **32** (2), 194-196.—2-Thiophen-trans-aldoxime (**I**) (cf. Schreiber, *Org. Synth.*, 1950, **31**, 108) is highly specific for Pd. The complex (palladium factor 0.2470) is formed quant. from chloride soln. at pH  $\geq 6.0$ . The complex can be dried at 110° without decomposition. **I** is used as a 2% (w/v) soln. in 95% ethanol. Excess of **I** is added to the Pd soln. (10 to 50 mg of Pd) acidified with HCl to pH 0.2 to 0.8. The complex is digested on a steam bath for 15 min. Interference is caused by  $Ag^+$ ,  $Au^{3+}$ ,  $Ru^{3+}$  and  $Os^{4+}$  on heating and by  $Sn^{2+}$  by reducing the yield. Interference by  $Pt^{4+}$  can be minimised by adding ammonium oxalate or omitting the steam-bath digestion;  $Ce^{4+}$  interfere, but not  $Ce^{3+}$ , but  $Ce^{4+}$  can be reduced by  $H_2O_2$ ;  $Cu^+$ ,  $Pb^{2+}$ ,  $Hg_2^{2+}$  and  $Tl^+$  form partially soluble chlorides and are oxidised first. The maximum error reported is -0.3%.

R. M. S. HALL

**4292. Spectrophotometric determination of palladium with quinoline-2-aldoxime.** Nobuichi Oi (Fac. of Engng, Toyama Univ., Takaoka). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1959, **80** (10), 1151-1153.—Quinoline-2-aldoxime reacts with Pd at pH  $> 5$ , and the yellow chelate is extracted with  $CHCl_3$ . The  $CHCl_3$  soln. has two absorption peaks at 365 and 460 m $\mu$ , and a linear working curve is obtained for  $< 70 \mu g$  of Pd in 10 ml of  $CHCl_3$  by the use of the 365-m $\mu$  peak. There is no interference from Ru, Rh, Ir, Ni, Co or Fe ( $< 1$  mg each); Cu and Pt ( $< 1$  mg each) are masked with EDTA soln. (5%) (1 ml).

K. SAITO

**4293. Critical study of the determination of platinum with benzyltrimethylphenylammonium chloride.** A. D. Westland and L. Westland (Dept. of Chem., Univ. of Ottawa, Canada). *Talanta*, 1960, **3** (4), 364-369.—The method of Ryan (*Anal. Abstr.*, 1957, **4**, 2217), which is based on the pptn. of bromoplatinate from hydrobromic acid soln. by means of this reagent, has been improved. The ppt. is now successively washed with dioxan and cyclohexane. Drying at a lower temperature (80° for 1 hr.) is then possible, minimising decomposition. Negligible amounts of Pt are removed by these reagents. The reagent concn. recommended (0.25% in the supernatant liquid) is lower than that suggested by Ryan. Full details are given for the procedures for platinum soln., chloroplatinate soln. and soln. previously fumed with  $H_2SO_4$ . The accuracy in the last case is within 0.5%.

R. M. S. HALL

**4294. Determination of water in metallurgical slags.** K.-H. Obst and H. Malissa (Max-Planck-Inst. f. Eisenforsch., Düsseldorf). *Arch. Eisenhüttenw.*, 1959, **30** (10), 601-603.—The sample is heated at 1450° in a quartz tube to expel the  $H_2O$ , which then reacts with  $CaC_2$  mixed with ignited sand (5:1). The acetylene formed burns to  $CO_2$ , which is determined by the decrease in conductivity produced when the  $CO_2$  is dissolved in an aq. alkali soln. The water content of the sample can thus be recorded automatically. Information is provided concerning the presence of hydroxyapatite in calcium phosphate slags; the sample must first be

shaken with 2% citric acid soln. to dissolve  $Ca(OH)_2$ , the presence of which leads to high values for the water content.

J. H. WATON

**4295. Rapid methods for determining the main elements in the concentrates and mother liquors in the manufacture of sea salt.** G. N. Babatschew (Res. Inst. for Building, Sofia, Bulgaria). *Z. anal. Chem.*, 1960, **173** (2), 121-125 (in German).—Rapid determinations of Fe, Ca, Mg, K, Na,  $Cl^-$  and  $SO_4^{2-}$  necessary in the control of sea-water evaporation are possible by combination of complexometric and ion-exchange techniques. Firstly, cations are retained on Wofatit KPS-200 ( $H^+$  form) and  $Cl^-$  and total anions are determined in the percolate. After elution of the resin with 2 N HCl, the Ca, Ca + Mg, and Fe are determined with EDTA (with fluorescein, Eriochrome black T, and salicylic acid, respectively, as indicator). The sum of Na and K is determined after exchange for Mg on Wofatit KPS-200 ( $Mg^{2+}$  form), while Na itself is pptd. as the zinc uranyl acetate. The Zn is titrated, after acidification, with EDTA (disodium salt) soln., with Eriochrome black T as indicator. Accuracy for  $Cl^-$  (3.5 to 38.5 mg),  $SO_4^{2-}$  (5 to 30 mg), Ca (4 to 32 mg), Mg (3 to 10%), Na (10 to 30 mg), K (10 to 30 mg), and Fe (3 to 15 mg) is within  $\pm 5\%$  in each case.

J. P. STERN

See also Abstracts—4092, Determination of P. 4094, Use of Solochrome green V as indicator. 4095, Use of chlorophenol-selenazine for  $Pd^{2+}$ . 4098, Indicator for Ca determination. 4104, Polarographic determination of Cu, Pb and Mo. 4321, Separation and detection of  $H_2O_2$ . 4340, Determination of sulphides. 4370, Trace metals in petroleum. 4398, Strontium in biological materials. 4403, Selenium in biological materials. 4465, Lead in pharmaceuticals. 4481, Nitrite in meat-curing brines. 4510, Nickel and  $Ni(CO)_4$  in air. 4557, Separation of phosphatides. 4572, Uranium in process streams. 4576, Determination of N in argon. 4594, Inclusions in steel. 4597, Detection of CO. 4624, Determination of U and Pu.

### 3.—ORGANIC ANALYSIS

*Determination of elements and radicals and of organic compounds not included in other sections. Organic industrial products, including petroleum and its products, fuels, detergents, volatile oils, cosmetics, dyestuffs, fibres, plastics, resins, paints, elastomers, leather, explosives.*

**4296. Developments in organic analysis.** M. Pesetz and M. Legrand (Centre de Rech. Roussel-Uclaf). *Bull. Soc. Chim. France*, 1960, (3), 453-461.—In this review, three trends in organic analysis are considered—(a) the reduction of sample size, exemplified by the Schöniger combustion in a closed vessel and subsequent determination of elements, and the process of "cryodiffusion" in which a small amount of volatile material is entrained in high vacuum into a liquid-nitrogen trap; (b) the use of colorimetric techniques, including the determination of compounds as hydroxamic acid deriv.; and (c) the development of polarimetric measurement (with Faraday cells and photomultiplier tubes). (80 references.) E. J. H. BIRCH



4297. Separation of analogous or isomeric compounds in classical polarography and oscillographic polarography. J. Tirouflet and E. Laviron (Fac. Sci., Dijon, France). *Z. anal. Chem.*, 1960, **173** (1), 43-50 (in French).—Many compounds that give polarographic waves too close to be resolved by classical polarographic techniques (e.g., *m*- and *p*-nitroanilines) may be resolved by derivative oscillographic polarography. In some cases in which resolution cannot be effected, satisfactory results can be obtained after conversion into more reactive derivatives. T. R. ANDREW

4298. Qualitative and quantitative analysis of organic compounds. Use of low-voltage mass spectrometry. C. J. Varsel, F. A. Morrell, F. E. Resnik and W. A. Powell (Univ. of Richmond, Va., U.S.A.). *Anal. Chem.*, 1960, **32** (2), 182-186.—The method described eliminates the use of simultaneous equations in quant. calculations and has a precision and accuracy about the same as those of normal mass spectrometry. Qualitatively, the method can be used to supplement the information obtained from a normal mass spectrum and it can also be used as a rapid means of obtaining the mol. wt. and ionisation potential of an organic compound. Fragment ions and low-sensitivity molecule-ion types interfere. K. A. PROCTOR

4299. Determination of deuterium in organic compounds by infra-red spectrophotometry. R. N. Jones and M. A. MacKenzie (Div. of Pure Chem., Nat. Res. Council of Canada, Ottawa, Canada). *Talanta*, 1960, **3** (4), 356-363 (in English).—The method of Trenner *et al.* (*Anal. Chem.*, 1956, **28**, 530) has been modified procedurally. Full details of the alterations in obtaining, collecting and transferring the water from the combustion to the absorption cell are given. The extinction at  $2520\text{ cm}^{-1}$  ( $\text{H}_2\text{O}$  band) is now measured with a double-beam i.r. spectrophotometer, with natural-abundance water as reference. This procedure obviates troubles due to temperature changes. R. M. S. HALL

4300. Radiometric analysis of tritiated organic compounds by means of vapour-phase chromatography. F. Cacace and Inam-ul-Haq (Inst. Pharm. Chem., Univ. Rome). *Science*, 1960, **131**, 732-733.—Volatile tritiated compounds are fractionated by means of vapour-phase chromatography and the radioactivity of the fractions is measured by means of a flow ionisation chamber. The effluent gases from the chromatographic column, having been passed through a conventional thermoconductivity cell for the usual analysis of compounds present in macroscopic quantities, are diluted with a current of the carrier gas in such a way that the total flow rate may be adjusted to a certain fixed value at which the ionisation chamber is calibrated. The necessity for heating the ionisation chamber is thus eliminated and substances such as chlorobenzene and anisole can be satisfactorily analysed. N. E.

4301. Techniques for the micro-combustion of substances labelled with carbon-14 and the measurement of the activity with carbon dioxide counters. M. A. Busellu, O. D'Agostino and C. Rossi (Lab. Chim. and Chim. Biol., Ist. Sup. di Sanità, Roma, Italy). *R.C. Ist. Sup. Sanit.*, 1960, **23** (1), 57-67.—Available techniques for micro-combustion and for the measurement of the activity with carbon dioxide counters are critically reviewed. The best combination of rapidity and accuracy is obtained

by using counters in the proportional region after micro-combustion by the method of Busellu *et al.* (*Anal. Abstr.*, 1960, **7**, 4300). (23 references.) E. C. APLING

4302. Carbon-hydrogen determination by gas chromatography. A. A. Duswalt and W. W. Brandt (Purdue Univ., Lafayette, Ind., U.S.A.). *Anal. Chem.*, 1960, **32** (2), 272-274.—The organic sample is burned in a stream of dry  $\text{CO}_2$ -free oxygen. The resulting  $\text{CO}_2$  and water vapour are passed through  $\text{CaC}_2$ , which converts the water vapour into acetylene. After concentration in a cold trap, the  $\text{CO}_2$  and acetylene are vaporised, introduced into the chromatographic system by the carrier gas (He), and measured in a thermal-conductivity cell. Symmetrical peaks are obtained, the areas for the  $\text{CO}_2$  and acetylene peaks being respectively proportional to the wt. of C and H in the original sample. The precision is 0.5 and 0.1% absolute for the C and H determinations, respectively, for sample sizes in the range of 2 to 6 mg. G. P. COOK

4303. Application of gas chromatography to micro-determination of carbon and hydrogen. O. E. Sundberg and C. Maresh (American Cyanamid Co., Bound Brook, N.J., U.S.A.). *Anal. Chem.*, 1960, **32** (2), 274-277.—The sample is burned to  $\text{CO}_2$  and  $\text{H}_2\text{O}$  with a mixture of  $\text{CuO}$  and copper at a temp. of  $750^\circ$  in an atmosphere of He. The water is then converted into acetylene in a tube of  $\text{CaC}_2$  and the gases are separated in a silica gel column, with He as carrier gas. The separated components are detected by thermal conductivity and their concn. recorded in terms of peak areas. The mean deviation of the results was  $\pm 0.54$  and  $0.21\%$  absolute for the C and H determinations, respectively. As little as 1.5 mg of sample can be analysed. G. P. COOK

4304. Determination of carbon and hydrogen in organic compounds. II. Efficiency of combustion catalysts. J. Horáček, J. Körbl and V. Pechánek (Chem. Inst., Czech. Acad. of Sci., Prague). *Mikrochim. Acta*, 1960, (2), 294-298 (in German).—Twenty-eight combustion catalysts have been studied for their efficiency in the combustion of a mixture of methane and O. The lowest temp. at which complete oxidation takes place has been found for each, and on this basis they have been divided into two groups. The first group comprises those that can bring about quantitative combustion below  $500^\circ$ , and the second group those that are ineffective even at  $650^\circ$ ;  $\text{Co}_3\text{O}_4$  was effective at  $311^\circ$  when made by pptn. and at  $345^\circ$  when made by ignition of the nitrate. Almost as efficient were a mixture of  $\text{Co}_3\text{O}_4$  and silver,  $\text{Fe}_2\text{O}_3$  with or without silver, and pptd.  $\text{CuO}$ . The results are of interest since steroids with an angular methyl group give methane on combustion. H. M.

4305. Rapid method for the micro-determination of carbon in organic substances. W. Stuck (Anal. Lab. Farbenfabriken Bayer A.-G., Werk Uerdingen, Germany). *Mikrochim. Acta*, 1960, (3), 421-428 (in German).—A modification of the procedure of Malissa (*Anal. Abstr.*, 1958, **5**, 1242) is described which enables it to be extended to the determination of major amounts (up to 79%) of C in organic compounds of all kinds. A single determination (5 to 10-mg sample) takes 10 to 15 min. and a precision of  $\pm 0.3\%$  is reported. T. R. ANDREW

**4306. Simultaneous micro-determination of carbon, hydrogen and nitrogen in nitro compounds.** E. I. Margolis and A. G. Shevkoptyas (School of Org. Chem., Moscow Univ.). *Vestn. Moskov. Univ.*, 1960, (1), 73-78.—The sample (3 to 8-mg) is mixed with the product obtained by decomposing silver permanganate at 500°, and slowly ignited in a quartz boat in a quartz ignition tube at 450° to 500° in a current of O for 20 to 25 min. Water is absorbed with anhydrous and  $\text{CO}_2$  with Ascarite;  $\text{NO}_2$  from the nitro groups is absorbed in two tubes containing a 2-cm layer of anhydrous, then a 5-cm layer of silica gel impregnated with a soln. of  $\text{K}_2\text{Cr}_2\text{O}_7$  in  $\text{H}_2\text{SO}_4$ , and a 3-cm layer of anhydrous; these tubes are placed between the tubes absorbing  $\text{H}_2\text{O}$  and  $\text{CO}_2$ . For all three elements the error is  $\pm 0.3\%$ . Amino N is oxidised to  $\text{NO}_2$  to the extent of 63 to 75%. C. D. KOPKIN

**4307. Rapid methods of micro-elementary analysis. XVII. Simultaneous micro-determination of carbon, hydrogen, mercury and halogen from a single sample of organic substance.** M. O. Korshun, N. S. Sheveleva and N. E. Gel'man (Inst. of Elementary Org. Compounds, Acad. Sci., USSR, Moscow). *Zhur. Anal. Khim.*, 1960, 15 (1), 99-103.—The method is based on igniting the substance in a stream of O and gravimetric determination of the four elements. Carbon, H and halogen are determined as described in "New Methods of Elementary Micro-analysis," Korshun and Ge'man, State Chem. Publ., M.-L., 1949, and Hg is collected in the combustion tube on silver and determined by the increase in weight. The error for Hg is  $\pm 0.7\%$  (abs.). Mercury nitrate is not formed during the determination of Hg in substances containing N. Heavy metals that do not form volatile salts with the halogen can also be determined.

A. BURWOOD-SMITH

**4308. Studies on oxygen determination in organic micro-analysis. I. Modified purification method of nitrogen gas.** Satoshi Mizukami, Tadayoshi Ieki and Kazue Numoto (Res. Lab., Shionogi & Co. Ltd., Imafuku, Amagasaki, Hyogo-ken, Japan). *Mikrochim. Acta*, 1960, (2), 183-187 (in English).—An improved purification tube, containing 20 g of Raney nickel (I) for removing traces of oxygen in nitrogen gas, is described. About 20 g of I prepared from 40 g of Raney alloy is poured into the tube with water. By opening the stopcock at the bottom of the tube the water is removed and I is dried for 3 hr. at 110° to 130°. It is claimed that oxygen is completely removed from the nitrogen gas at room temp. and that one tube of I can be employed for about 6 to 9 months.

**II. The micro-analysis of oxygen by decrease in the quantity of anhydro-iodic acid.** Satoshi Mizukami and Tadayoshi Ieki. *Ibid.*, 1960, (2), 188-191 (in English).—The gravimetric method described for the determination of oxygen in organic compounds is based on the quantitative reaction between carbon monoxide and anhydro-iodic acid (II). II (100 to 200 mesh) (4 to 4.5 g) is packed in a glass funnel, which is introduced into the oxidation tube. The oxygen in the sample is calculated from the decrease in weight of II; results are tabulated. The oxidation apparatus and glass funnel are illustrated. B. B. BAUMINGER

**4309. Acoustic control of combustion in the Dumas determination of nitrogen.** K. Eder (Micro-anal. Lab., Chem. Dept., Univ. Geneva). *Mikrochim. Acta*, 1960, (2), 197-199 (in German).—The efficiency of combustion is dependent on the speed of gas

flow, and this can be observed acoustically. The sound produced by a bubble passing through a bubble counter can be detected with an ordinary gramophone pick-up having a stiff bent wire in place of the stylus. The wire is clipped to the bubble counter with a strip of thin metal and a rubber band or spring, and the sound is amplified and passed to a loud-speaker. H. M.

**4310. Rapid micro-determination of nitrogen in organic compounds with trico-balt tetroxide as combustion catalyst.** M. Večeka and L. Synek (Micro-anal. Lab., VÚOS, Pardubice-Rybitví, Czechoslovakia). *Mikrochim. Acta*, 1960, (2), 208-219 (in German).—The sample (1.5 to 4 mg) is weighed into a platinum boat and transferred to a quartz combustion tube. A stream of  $\text{CO}_2$  enriched with O produced by electrolysis of 25%  $\text{H}_2\text{SO}_4$ , is passed through the tube and the sample is volatilised with an electric oven at 750° to 900°. The mixture of gases passes through a catalyst mass of  $\text{Co}_3\text{O}_4$  on corundum at 700°, thence through a layer of copper particles at 550°. The copper removes excess of O and the N is measured volumetrically with a nitrometer. Details of the preparation of the catalyst are given, and the apparatus is illustrated and described. The method is claimed to be more accurate and more rapid than the usual CuO method. H. M.

**4311. Colorimetric micro-Kjeldahl method with direct nesslerisation for routine determination of nitrogen (nitro and nitroso groups excepted).** H. C. Burck (Inst. physiol. Chem. u. Physikochem., Univ. Kiel, Germany). *Mikrochim. Acta*, 1960, (2), 200-203 (in German).—The sample is oxidised with conc.  $\text{H}_2\text{SO}_4$  and 30%  $\text{H}_2\text{O}_2$  soln. in a Kjeldahl flask calibrated at 50 ml, and the soln. is made up to the mark. A suitable aliquot containing 20 to 50  $\mu\text{g}$  of N is transferred to a 50-ml flask, 2 ml of Nessler soln. is added and the soln. is made up to volume. After exactly 15 min. the extinction is measured at 450 m $\mu$  and, after deduction of a blank, is compared with a calibration curve. The method is claimed to be rapid and accurate (within  $\pm 1\%$ ). H. M.

**4312. New method for the iodimetric determination of halogens in organic substances.** E. Meier (Micro-anal. Lab., Weizmann Inst. of Science, Rehovoth, Israel). *Mikrochim. Acta*, 1960, (2), 204-207 (in German).—The sample (1 to 3 mg) is burnt in a stream of O in a quartz tube packed with platinised asbestos at a temp. of 1050°. The issuing gases pass through a tube containing solid AgI at a temp. of 200°, where iodine is liberated. The iodine is absorbed in 20% NaOH soln. in a tube packed with glass balls. The soln. is washed out and oxidised with Br to  $\text{IO}_3^-$ , which liberate iodine from acidified KI soln., and the iodine is titrated with 0.005 N  $\text{Na}_2\text{S}_2\text{O}_3$ . The accuracy claimed is within  $\pm 1\%$ . Sulphur interferes. H. M.

**4313. The use of nitrite in the determination of halogen in organic compounds.** W. J. Kirsten (Res. Lab., Pharmacia Ltd., Uppsala, Sweden). *Mikrochim. Acta*, 1960, (2), 272-274 (in English).—The Cl<sup>-</sup> and Br<sup>-</sup> produced in the combustion of the organic sample, carried out either by flask combustion or combustion and subsequent hydrogenation procedures, are treated with 1 ml of  $\text{NaNO}_2$  soln. (2.5%). The excess of  $\text{NaNO}_2$  is reduced with 2 ml of hydrazine sulphate soln. (2.5%) and the soln. is titrated potentiometrically with  $\text{AgNO}_3$  soln. No results are given. B. B. BAUMINGER

**4314. Organic elementary analysis with a micro-bomb. V. Determination of fluorine in organic compounds by titration with aluminium chloride.** Asaji Kondo (Org. Chem. Lab., Tokyo Inst. Tech., Meguro-ku, Tokyo). *Japan Analyst*, 1959, **8** (9), 561-563.—The sample ( $\approx 15$  mg) is decomposed by heating with  $\text{Na}_2\text{O}_2$  ( $\approx 0.5$  g) and glucose ( $< 20$  mg) at  $500^\circ$ , then dissolved in water (20 ml); the pH is adjusted to 6 to 6.5 and the product is titrated with  $0.01 M \text{AlCl}_3$  in a hot soln., with Eriochrome black T as indicator. For  $< 3$  mg of F<sup>-</sup>, the indicator error is significant and the use of an empirical diagram is recommended for correction. The adjustment of pH must be made carefully with  $0.1 N \text{HCl}$  and  $\text{NaOH}$  in a saturated  $\text{NaCl}$  soln. at  $95^\circ$ . The error is  $\approx 0.5\%$ . K. SAITO

**4315. Techniques useful for sodium biphenyl determination of micro quantities of organic chlorine.** R. C. Blinn (Univ. Calif., Citrus Exp. Sta., Riverside, U.S.A.). *Anal. Chem.*, 1960, **32** (2), 292-293.—A rapid convenient method is described for the preparation and use of sodium biphenyl reagent for the reduction of organic halogens to halides. Recoveries of added Cl to various chlorinated insecticides and acaricides ranged from 96 to 105% at the 200- $\mu\text{g}$  level. G. P. COOK

**4316. Quantitative micro-determination of boron in organic compounds by ignition in oxygen.** S. I. Obtemperanskaya and V. N. Likhoshershtova (School of Org. Chem., Moscow Univ.) *Vestn. Moskov. Univ.*, 1960, (1), 57-59.—Fold the sample inside a filter-paper, leaving a strip of paper free, and attach this to a platinum wire fixed to the ground glass stopper of a 250-ml flask. Place 5 ml of  $0.5 N \text{NaOH}$  and 6 ml of water in the flask, displace the air with  $\text{O}_2$ , ignite the free strip of paper and place the sample in the flask, holding the stopper firmly in place. Set aside for 15 to 20 min. after burning is complete. Rinse the stopper, add a drop of methyl red, and then  $0.5 N \text{H}_2\text{SO}_4$  till the soln. is slightly acid, boil for a few minutes to remove  $\text{CO}_2$ , neutralise with  $0.02 N \text{NaOH}$ , add  $0.5$  g of mannitol and 3 drops of phenolphthalein, and titrate the boric acid with  $0.02 N \text{NaOH}$ . The error is  $\pm 0.3\%$  abs. C. D. KOPKIN

**4317. Micro-determination of selenium in organic compounds containing chlorine, bromine or sulphur.** A. S. Zabrodina and A. P. Khlystova (School of Org. Chem., Moscow Univ.). *Vestn. Moskov. Univ.*, 1960, (1), 69-72.—The basic procedure is as already described (Zabrodina and Bagreeva, *Anal. Abstr.*, 1959, **6**, 2197). In the presence of Cl, conc.  $\text{HCl}$  (4 ml) is added to the soln. of  $\text{H}_2\text{SeO}_3$  formed by dissolving the  $\text{SeO}_2$  obtained on ignition, and the soln. is boiled to a vol. of 10 or 15 ml to reduce  $\text{H}_2\text{SeO}_4$  (formed by the chlorine oxidation of  $\text{H}_2\text{SeO}_3$ ) and to remove free Cl. The iodimetric titration is carried out by the usual method. In the presence of Br, the  $\text{SeO}_2$  is dissolved in a soln. of 2 ml of 25%  $\text{KBr}$  and 0.5 ml of conc.  $\text{HCl}$  made up to 6 or 7 ml; the soln. is then boiled till colourless, 3 ml of conc.  $\text{HCl}$  is added, the soln. is evaporated to 10 to 15 ml, 3 drops of ethanolic acetanilide soln. are added, and the determination is completed by the usual procedure. In the presence of S, the sample is ignited in the presence of a platinum contact and the  $\text{SeO}_2$  and  $\text{SO}_2$  are absorbed and dissolved in 6 or 7 ml of water containing 8 to 10 drops of  $\text{H}_2\text{O}_2$ ; 4 ml of  $\text{HCl}$  is added and the soln. is boiled for 30 min., cooled, and titrated. The error is  $\pm 0.3\%$ . C. D. KOPKIN

**4318. Colour reaction of mercapto groups with 2:6-dibromo-p-benzoquinonechlorimine.** Shozo Kamiya (National Hyg. Lab., Tamagawa-yoga, Setagaya-ku, Tokyo). *Japan Analyst*, 1959, **8** (9), 596-597.—2:6-Dibromo-p-benzoquinonechlorimine (I) in ethanol or dioxan gives a characteristic coloration with thioketones which can be enolated. Aliphatic mercapto compounds give a yellow colour, aromatic and heterocyclic mercapto compounds orange, thiourea derivatives violet, and xanthates yellowish-green to purple. The sample ( $\approx 1$  mg) in ethanol (0.2 ml) is mixed with one drop each of  $0.01 N \text{NaOH}$  and I in ethanol (0.1%). K. SAITO

**4319. Detection of primary alkyl halides by a spot reaction.** F. Feigl, V. Anger and D. Goldstein (Lab. Prod. Mineral, Min. Agric., Rio de Janeiro). *Mikrochim. Acta*, 1960, (2), 231-234 (in German).—When primary alkyl halides are heated with  $\text{Na}_2\text{S}_2\text{O}_8$ , Bunte's salt,  $\text{SO}_3(\text{SR})\text{ONa}$ , is formed. This decomposes between  $160^\circ$  and  $180^\circ$  to give  $\text{SO}_2$ , which can be detected. The sample is mixed with  $\text{Na}_2\text{S}_2\text{O}_8$  in a micro test-tube and heated in an oil bath at  $100^\circ$ . The temp. is gradually raised, and at  $140^\circ$  a piece of Congo red paper moistened with  $10\% \text{H}_2\text{O}_2$  soln. is placed over the mouth of the tube. A blue spot on the red paper at  $160^\circ$  to  $180^\circ$  denotes a positive reaction. As little as  $5 \mu\text{g}$  of certain substances can be detected. H. M.

**4320. Assay of technical di-(2-chloroethoxy)-methane.** K. Hetnarska and S. Piotrowski (Anal. Dept., Inst. of Organ. Industry, Warsaw). *Chem. Anal., Warsaw*, 1959, **4** (5-6), 909-913.—A method of analysis of technical di-(2-chloroethoxy)methane (I) was developed which consists of (i) determination of the total chlorine content after hydrolysis with sodium by the method of Stiepanow, and (ii) determination of the chlorine in 2-chloroethanol (II) (separated by washing out with water) after previous hydrolysis with aq.  $\text{KOH}$  soln. Owing to the solubility of acetal in water, an empirical correction of  $-0.70\%$  of chlorine was applied when calculating the amount of II. The amount of I was obtained by difference. The mean absolute error was  $\approx \pm 0.40\%$ . L. SMAKOWSKI

**4321. Separation and identification of peroxides by paper chromatography.** J. Cartlidge and C. F. H. Tipper (Dept. of Inorg. and Phys. Chem., Univ. Liverpool). *Anal. Chim. Acta*, 1960, **22** (2), 106-110.—The examination of  $\text{H}_2\text{O}_2$  and 27 aliphatic peroxides is reported. Comparison of the  $R_F$  values given by experiments with a glycol-treated paper with three different sets of stationary and mobile phases shows that the class of the peroxide may be distinguished and that the members of each class may be identified in most cases. The more non-polar peroxides (e.g., dialkyl peroxides) were better resolved by the use of silicone-treated paper. The limit of detection of  $\text{H}_2\text{O}_2$  on untreated or silicone-treated paper was  $20 \mu\text{g}$ , and with glycol-treated paper was  $0.4 \mu\text{g}$ . In this latter case the limits of detection of  $\text{H}_2\text{O}_2$ , *tert*-butyl hydroperoxide and *n*-heptyl hydroperoxide were 0.4, 10 and  $20 \mu\text{g}$ , respectively. The treatment of unknown mixtures is discussed. E. G. CUMMINS

**4322. Metallic zinc as a catalyst for quantitative acetylation of some hydroxy compounds.** D. Kyriacou (Anal. Chem. Dept., Aerojet-General Corp., Sacramento, Calif., U.S.A.). *Anal. Chem.*, 1960, **32** (2), 291-292.—The presence of metallic zinc greatly increases the rate of acetylation, by

acetyl chloride, of compounds such as poly(propylene glycol) and glycerol ricinoleate. G. P. COOK

**4323. Separation of lower aliphatic alcohols by paper chromatography and their quantitative determination.** G. E. Zaikov (Inst. of Chem. Phys., Acad. Sci., USSR, Moscow). *Zhur. Anal. Khim.*, 1960, **15** (1), 104-108.—A quantitative determination of methyl, ethyl, propyl and butyl alcohols is carried out by paper chromatography of the corresponding esters of 3:5-dinitrobenzoic acid. The method employed is that described by Deigh (*Nature*, 1952, **169**, 706). Accurate determination is possible in the presence of 15 to 20% of  $H_2O$  and 80 to 85% of hexane. A. BURWOOD-SMITH

**4324. Titrimetric analysis of 3:5-dinitrobenzoate derivatives.** W. T. Robinson, jun., R. H. Cundiff, A. J. Sensabaugh and P. C. Markunas (R. J. Reynolds Tobacco Co., Winston-Salem, N.C., U.S.A.). *Talanta*, 1960, **3** (4), 307-310 (in English).—Alcohols and symmetrical ethers are determined by titration of their 3:5-dinitrobenzoate derivatives with 0.01 N tetrabutylammonium hydroxide. The derivative should be dissolved in pyridine and heated under reflux before titration, which is conducted potentiometrically under nitrogen. Of 24 alcohols and 1 ether titrated, the results (average of at least 2 determinations) range from 97.96 to 103.10%, the greater number being between 99.5 and 100.5%. R. M. S. HALL

**4325. Identification and determination of alcohols in solution with vanadium oxinate as colour reagent.** Senjiro Maruta and Fumio Iwama (Chem. Dept., Yamanashi Univ., Motoyanagi-cho, Kofu). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1959, **80** (10), 1131-1133.—Vanadium oxinate in xylene or acetic acid produces various colours with alcohols; the absorption curve has no peak and the extinction-concn. diagram (e.g., at 640 m $\mu$ ) is not linear, although reproducible. The error of a photometric determination of an individual alcohol is 4%. Chromatographic separation of normal alkyl alcohols ( $C_2$  to  $C_{10}$ ) and polyhydric alcohols was unsuccessful in dil. acetic acid and in a mixture of acetic acid, water and petroleum hydrocarbon (boiling-range 140° to 170°), although individual alcohols gave characteristic  $R_F$  values. K. SAITO

**4326. Gas-chromatographic analysis of alcohols as esters of nitrous acid.** F. Drawert and G. Kupfer (Bundesforschungsanst. f. Rebenezüchtung Geilweilerhof, Abt. Biochem. u. Physiol., Siebeldingen über Landau, Pfalz). *Angew. Chem.*, 1960, **72** (1), 33-34.—The sample is acidified with tartaric acid (50% by wt.) and injected into a reaction zone containing a mixture of  $NaNO_2$  and Sterchamol (1:1). The nitrite esters formed are swept through a column of silicone grease and Sterchamol (3:10) by a stream of  $H_2$  (35 ml per min.). Relative retention vol. (benzene = 1.00) on columns operating at 70° and 100° are reported for alcohols from methanol to isoamyl alcohol. T. R. ANDREW

**4327. The effect of some organic solvents on the turbidimetric analysis of tert.-butyl alcohol.** M. R. F. Ashworth (Inst. for Org. Chem., Univ. of the Saar, Saarbrücken, Germany). *Mikrochim. Acta*, 1960, (2), 175-182 (in English).—Conditions have been studied for the turbidimetric determination of tert.-butyl alcohol in liquids poorly miscible with water. The method is based on the reaction with a mercuric sulphate- $H_2SO_4$  reagent recently described by

Ashworth (*Mikrochim. Acta*, 1959, 506). Good results are obtained by using 50 to 70% acetic acid as solvent. B. B. BAUMINGER

**4328. Determination of 2-ethoxyethanol and accompanying water, ethanol and ethanediol.** E. M. Pereplechikova, V. S. Étlis and A. A. Kalugin. *Zavod. Lab.*, 1960, **26** (2), 154-156.—*Determination of ethanediol*—The sample of impure 2-ethoxyethanol (containing > 0.02 g of ethanediol) is treated with 15 ml of water and then with 5 ml of 0.1 M  $HIO_4$ , prepared by mixing a soln. of 10.7 g of  $Na_2H_2IO_7$  in 20 ml of water with 100 ml of N  $H_2SO_4$  and 380 ml of water. After 10 min., 5 ml of 20% KI soln. is added and after another 5 min. the soln. is titrated with 0.05 N  $Na_2S_2O_3$  in the presence of starch. A blank titration in the presence of 5 drops of 3% formaldehyde soln. (since the oxidation of ethanediol in the sample soln. yields formaldehyde) is carried out at the same time. If the vol. required for titrating the sample soln. is < 60% of that required for the blank, the experiment should be repeated with a smaller sample wt. *Determination of 2-ethoxyethanol*—The method is based on that of Siggia et al. (*Anal. Abstr.*, 1958, **5**, 2232). *Determination of ethanol*—A stream of N at a standard rate (0.5 litre in 25 min.) is passed through a tube containing the sample ( $\approx 1$  g) immersed in a boiling-water bath and then through two absorption vessels each containing 10 ml of 0.1 N  $K_2Cr_2O_7$  and 5 ml of 55%  $H_2SO_4$ . After the passage of 0.5 litre of N, the contents of the absorption vessels are poured into a 250-ml graduated flask, which is then stoppered and set aside, with occasional shaking, for 30 min. Dry KI (1 g) is added and the soln. is titrated with 0.1 N  $Na_2S_2O_3$  after 5 min. The method is standardised by use of mixtures containing known amounts of ethanol. The determination of water is carried out by Fischer's method. Satisfactory results were obtained with mixtures containing 0.35 to 1.49% of ethanediol, 1.53 to 2.18% of ethanol, and 0.65 to 0.92% of water. G. S. SMITH

**4329. Micro-determination of glycol ethers.** G. Kainz (Anal. Inst., Univ. Wien). *Mikrochim. Acta*, 1960, (2), 254-260 (in German).—Compounds with the grouping  $-O-CH_2-CH_2-OH$  are decomposed by HI to give a mixture of ethyl iodide and ethylene. The ethyl iodide is determined volumetrically with  $AgNO_3$  soln., and the ethylene with a nitrometer. The sample is dissolved by warming in phenol in a methoxyl apparatus and is then heated with HI. A stream of  $CO_2$  carries the evolved gases through a washer containing red phosphorus and  $CdSO_4$  soln., thence through an absorber containing standard  $AgNO_3$  soln. in glacial acetic acid and finally into a nitrometer. The excess of  $AgNO_3$  soln. is titrated with standard KI soln., with starch and iodine in ethanol as indicator. The nitrometer serves as an indicator of the progress of the reaction, as well as to measure the volume of the ethylene. About 1 hr. is required for the decomposition of glycol ethers, whereas ethanediol reacts within 10 min. H. M.

**4330. Oxidation of glycol with periodic acid in the presence of boric acid.** J. Plouquin and C. Neau (Lab. de Chim., Fac. de Médecine, Nantes, France). *Compt. Rend.*, 1960, **250** (12), 2211-2212.—During the first few minutes,  $H_2BO_3$  accelerates the oxidation of 0.1 M glycerol by a ten-fold excess of 0.1 N  $HIO_4$  at 25° and pH 6.3, but has no such effect at pH 1.6. Activation also occurs (during the first 30 min. only) at pH 8.2, but the total rate of



oxidation is low because of the inhibitory effect of the alkali. The mol. ratio of  $H_2BO_3$  to glycerol should be from 0.5 to 2. The results confirm the conclusions of Malaprade and of Fleury and Courtois (*Bull. Soc. Chim. France*, 1934, 1, 833; 1943, 10, 245) that  $H_2BO_3$  accelerates slightly the oxidation of sugars and acyl hexitols by  $IO_3^-$  at constant pH. W. J. BAKER

**4331. Micro-determination of sugars by means of a copper compound of trihydroxyglutaric acid.** A. V. Ablov and D. G. Bat'yr (Acad. Sci. USSR, Moldavsky Branch, Kishinev). *Zhur. Anal. Khim.*, 1960, 15 (1), 112-114.—The method has the advantage of strict proportionality between the amount of sugar and the number of ml of permanganate necessary for the indirect titration of cuprous oxide. The method makes possible the determination of glucose, fructose, galactose, xylose, maltose and sucrose with high accuracy. *Procedure*—Into a series of tubes put  $n$  ml of sugar soln. (containing 0.1 to 9 mg of sugar) and 3 ml of  $H_2O$ . To these add 3 ml each of reagent A (40 g of  $CuSO_4 \cdot 5H_2O$  in 1 litre of  $H_2O$ ) and reagent B (128 g of trihydroxyglutaric acid and 207 g of NaOH in 1 litre of  $H_2O$ ). Immerse the tubes in boiling water for 6 min., then cool. Pour each soln. through a glass filter, wash each residue with warm  $H_2O$ , transfer to a small tube and dissolve the cuprous oxide in 3 to 5 ml of a soln. containing 86 g of  $(NH_4)_2SO_4 \cdot Fe_2(SO_4)_3 \cdot 24H_2O$  and 108 ml of conc.  $H_2SO_4$  per litre of  $H_2O$ , transfer to a filter and wash with cold water. The filtrate containing  $Fe^{2+}$  is titrated with  $KMnO_4$  soln. (0.01 to 0.2 N) from a micro-burette until the colour changes from green to pale pink. A. BURWOOD-SMITH

**4332. Classification of fine structural characteristics in cellulose by infra-red spectroscopy. Use of potassium bromide pellet technique.** F. G. Hurtubise and H. Krässig (Industrial Cellulose Res., Ltd., Hawkesbury, Ontario, Canada). *Anal. Chem.*, 1960, 32 (2), 177-181.—It has been shown that i.r. spectroscopy can be used as the basis of a routine analytical method for classifying cellulose samples according to their fine structural characteristics. The potassium bromide pellet technique was particularly useful for studying the effect of mercerisation. K. A. PROCTOR

**4333. Quantitative analysis of acetic acid-acetic anhydride mixtures in the near-infra-red region. A statistical study.** J. E. Fernandez, R. T. McPherson, G. K. Finch and C. D. Bockman (Tennessee Eastman Co., Kingsport, U.S.A.). *Anal. Chem.*, 1960, 32 (2), 158-162.—Acetic acid in acetic anhydride in concn. up to 10% can be determined rapidly by the method described, in which the untreated sample is scanned between 1450 and 1600  $m\mu$ . In the range 0 to 7% of acetic acid neither the accuracy nor precision is affected by the concn. of the anhydride, and in this range the standard deviation is 0.16 (16 degrees of freedom). The method is more precise than the standard aniline and triethanolamine methods. K. A. PROCTOR

**4334. Determination of glyoxylic acid with resorcinol and its relevance to periodate oxidation.** M. Pesez and J. Bartos (Centre de Rech., Roussel-Uclaf). *Bull. Soc. Chim. France*, 1960, (3), 481-482.—Glyoxylic acid reacts with resorcinol in  $H_2SO_4$  to form 2:2':4:4'-tetrahydroxydiphenyl-acetic lactone, which is colourless but gives a violet colour with alkali, and subsequently gives an orange

colour on contact with air. If the colourless soln. is made alkaline with ethanolic KOH, the violet colour is sufficiently insensitive to air oxidation to enable spectrophotometric readings to be made. Beer's law is obeyed from 20 to 100  $\mu g$ . *Procedure*—To 1 ml of aq. glyoxylic acid soln. (20 to 100  $\mu g$ ) is added 2 ml of 1% resorcinol in  $H_2SO_4$  (3:7). The soln. is heated on a water bath for 5 min., cooled, and extracted with ethyl acetate. To 1 ml of the extract is added 4 ml of ethanol and 0.5 ml of N ethanolic KOH. The extinction is determined after 10 min. at 550  $m\mu$ . A standard soln. of glyoxylic acid is prepared by periodate oxidation of tartarate. In periodate-oxidation media (at pH 10) the excess of periodate is destroyed with ethanediol, and the iodate formed is pptd. with Ag before the determination. Glyoxylic acid, itself rapidly oxidised with periodate between pH 3 and 7, is oxidised by < 3% in 1 hr. at pH 10. The method is applied to the periodate oxidation of mucic acid.

E. J. H. BIRCH

**4335. A method for the oxidative determination of diacetyl.** F. Wolf (VEB Chem. Fabrik Miltitz, Leipzig, Germany). *Z. anal. Chem.*, 1960, 172 (6), 413-423 (in German).—The influence of pH, reaction time, temp. and concn. of  $H_2O_2$  and diacetyl (I) on the oxidation of I to acetic acid has been studied. Reaction is most rapid in alkaline soln., though an alternative procedure for neutral or acid soln. is given. Under the conditions specified, no decomposition of acetic acid occurs. Ethyl methyl ketone and ethanol, if present, do not interfere. *Procedure in alkaline solution*—Pipette 20 ml of 0.5 N aq. KOH and 2 ml of 30%  $H_2O_2$ , free from organic stabilisers, into a 100-ml flask. Add 10 ml of aq. 3% soln. of I down the side of the flask, stopper and swirl. After 5 min., rinse down the stopper and flask with  $H_2O$ ; back-titrate with 0.5 N  $H_2SO_4$  to thymol blue, with a titrated sample for comparison. Titre less blank  $\times 2.152$ /wt. of I = I (%). The error for 300 mg of I was  $\pm 0.3\%$ . P. D. PARR-RICHARD

**4336. Mass-spectrometric studies. II. Saturated normal long-chain esters of ethanol and higher alcohols.** R. Ryhage and E. Stenhagen (Karolinska Inst., Stockholm). *Ark. Kemi*, 1959, 14 (6), 483-495.—The compounds studied include five esters of *n*-docosanol and ethyl and butyl *n*-octadecanoate. **III. Esters of saturated dibasic acids.** R. Ryhage and E. Stenhagen. *Ibid.*, 1959, 14 (6), 497-509.—Some esters of normal and methyl-substituted dibasic acids containing up to 22 C atoms have been studied.

**4337. The polarography of amidines.** P. O. Kane (May & Baker Ltd., Dagenham, Essex, England). *Z. anal. Chem.*, 1960, 173 (1), 50-56 (in English).—The behaviour of 20 amidines has been studied in buffer soln. of pH 6.7 and pH 9.2. Aliphatic and arylaliphatic amidines show no wave in the range 0 to -1.9 V vs. the S.C.E.; phenoxacetamidines are reduced to the phenol and acetamide at  $E_1$  -1.4 to -1.74 V (6 compounds), and aromatic amidines are reduced to benzylamine and  $NH_3$  at  $E_1$  -1.45 to -1.65 V (8 compounds). No significant difference in  $E_1$  is found between the two pH values. T. R. ANDREW

**4338. Colorimetric method for the determination of  $\alpha$ -aminonitriles.** A. Szwczuk (Dept. of Biochem., Inst. of Immunology and Exp. Therapy, Wrocław). *Chem. Anal., Warsaw*, 1959, 4 (5-6), 971-979.—A simple and rapid colorimetric method

of determination of small amounts of  $\alpha$ -aminonitriles (0.01 to 0.1  $\mu$ mole per ml) is based on reaction with Br in acid medium in closed tubes at 37° for 1 hr. Under these conditions a substance (probably CNBr) is formed, that gives a red colour with a soln. of benzidine hydrochloride in pyridine; 0.0001 N KCN was used as standard. The method can be used for the determination of  $\alpha$ -aminonitriles in the presence of their acyl derivatives. Inorganic cyanides give this reaction instantaneously,  $\alpha$ -aminobutyronitrile only after 1 hr., so that it is possible to determine each of these separately in mixtures. The presence of cysteine and glutathione in concn.  $> 10^{-4}$  M causes low results. The method is specific for  $\alpha$ -aminonitriles, even in the presence of  $\beta$ -aminonitriles. L. SMAKOWSKI

**4339. Polarography of  $\alpha$ -hydroxyimino acids.** Jun-Ichi Nakaya, Kan Mori, Hiroshi Kinoshita and Shin-Ichi Ono (Coll. of Gen. Educ., Osaka Prefectural Univ., Sakai). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1959, **80** (11), 1282-1284.—The reduction potential of  $\alpha$ -hydroxyimino acids was compared polarographically with that of other oximes at various pH values and its use for quant. analysis is discussed. These acids have reduction potentials of  $-0.489$  to  $-0.713$  V vs. the S.C.E. in 10% ethanol at pH 1, the waves corresponding to a 4-electron reduction. The type of acid having an undissociated carboxyl group has a max. wave height at a pH near the pK value of the carboxyl group, and the optimum pH for quant. analysis is 3 to 4. At a given pH the wave height is proportional to concn.  $< 0.01$  M. K. SAITO

**4340. Complexometry in organic analysis. VIII. Determination of some derivatives of thiourea (determination of sulphides).** B. Buděšínský, E. Vaníčková and J. Körbl (Res. Inst. for Pharm. and Biochem., Prague). *Coll. Czech. Chem. Commun.*, 1960, **25** (2), 456-460 (in German).—The cadmium-EDTA complex (I), yields CdS quant. on heating with sol. sulphides in an alkaline medium. Some derivatives of thiourea react similarly. After the separation of CdS the liberated EDTA is titrated with  $\text{CaCl}_2$  soln., with methylthymol blue as indicator. The reaction of thiourea and its derivatives with I is accelerated by the presence of certain reducing agents (e.g., hydrazine). *Procedure for thiourea deriv.*—Dissolve the sample ( $\approx 0.80$  milli-equiv.) in 1.25 M NaOH (10 ml), add 7 M hydrazine (5 ml) and 0.25 M I [dissolve 93 g of EDTA (disodium salt) in 400 ml of  $\text{H}_2\text{O}$ , add 70 g of cryst.  $\text{CdSO}_4$ , mix for 5 min. and add in portions 34 g of anhyd.  $\text{Na}_2\text{CO}_3$ ; filter after 2 to 3 hr. and dilute the filtrate with  $\text{H}_2\text{O}$  to 1 litre] (10 ml) and heat for 30 min. (for thiourea, acetylthiourea or thiopentone) or 180 min. (for nicotinaldehyde thiosemicarbazone hydrochloride or *p*-acetamidobenzaldehyde thiosemicarbazone). Cool, filter off the ppt. and wash it with  $\text{H}_2\text{O}$  (50 ml); dilute the filtrate to 150 ml, add 5 ml of aq.  $\text{NH}_3$ - $\text{NH}_4\text{Cl}$  buffer soln. (pH 10) and methylthymol blue and titrate with 0.05 M  $\text{CaCl}_2$  to a blue end-point. Deduct a blank. *Procedure for sulphides*—To 5 ml of a soln. of  $\text{Na}_2\text{S}$  ( $\approx 0.35$  mM) add 0.25 M I (10 ml) and 0.5 to 2 M NaOH (5 ml), heat for 15 min. on a water bath and proceed as described above;  $\text{SO}_3^{2-}$ ,  $\text{S}_2\text{O}_3^{2-}$  and  $\text{SCN}^-$  do not interfere. Accuracies of  $\pm 0.3\%$  for  $\text{S}^{2-}$  and  $\pm 1.4\%$  for thiourea deriv. were achieved. J. ZÝKA

**4341. Paper chromatography of derivatives of ethylenebisdithiocarbamic acid.** G. D. Thorn and

R. A. Ludwig (Pesticide Res. Inst., Dept. of Agric., London, Canada). *Rec. Trav. Chim. Pays-Bas*, 1960, **79** (2), 160-163 (in English).—Ascending paper partition chromatography of the oxidation products of disodium ethylenebisdithiocarbamate (I) with solvents containing butanol with admixtures of ethanol, benzene, acetic acid, pyridine, water or alkaline buffers has been studied. Two indicator sprays for the derivatives were used, viz, Feigl's iodine- $\text{NaN}_3$  reagent, which gives white spots on a blue ground, and Grote's reagent (*J. Biol. Chem.*, 1931, **93**, 25) with which I gives an orange, ethylenethiuram sulphide (II) a yellow-green, and ethylenethiourea (III) a blue spot. The position of sulphur was detected by u.v. spectroscopy of ethanol eluates of the sectioned paper (Heatley and Page, *Anal. Chem.*, 1952, **24**, 1854).  $R_F$  values for I, II and III in nine solvent mixtures are reported, the most useful being butanol-ethanol-water (120:33:57). The method may be used for the semi-quant. determination of oxidation products in I. E. J. H. BIRCH

**4342. Volumetric determination of some organophosphorus halidates and pyroester compounds using a peroxide reagent.** S. Sass, I. Master, P. M. Davis and N. Beitsch (Chem. Res. Div., Army Chem. Center, Md., U.S.A.). *Anal. Chem.*, 1960, **32** (2), 285-287.—The method is based on the stoichiometric reaction of alkoxy phosphorus halidates and anhydrides with peroxide. The sample is added to an excess of alkaline peroxide (pH 10) and, after a few minutes, the soln. is acidified with  $\text{H}_2\text{SO}_4$ . Potassium iodide is then added and the liberated iodine is titrated with  $\text{Na}_2\text{S}_2\text{O}_3$  soln. Results are tabulated for some alkyl phosphonofluoridates, pyrophosphonates, and alkyl phosphorofluoridates and pyrophosphates; the accuracy and precision are within  $\pm 1\%$ . G. P. COOK

**4343. Determination of tributyl phosphate in Mepasin (kerosine) by flame photometry.** J. Malinowski (Anal. Dept., Inst. of Nuclear Res., Warsaw). *Chem. Anal., Warsaw*, 1959, **4** (5-6), 939-945.—An air-acetylene flame and the TI-535 filter were used with the standard equipment of the Zeiss flame photometer, Model III. Calibration curves for different concn. ranges of tributyl phosphate are given. L. SMAKOWSKI

**4344. Refractometric determination of mutual solubility as a function of temperature. Tributylphosphine oxide and water.** C. E. Higgins and W. H. Baldwin (Chem. Div., Oak Ridge Nat. Lab., Tenn., U.S.A.). *Anal. Chem.*, 1960, **32** (2), 233-236.—By measuring refractive indices it has been shown that the mutual solubilities of water and tributylphosphine oxide are inversely temperature-dependent. The technique should prove generally applicable for the measurement of solubility and distribution as a function of temperature.

K. A. PROCTOR

**4345. Effect of centrifugation on solution temperature and solubility of tributyl phosphate and tributylphosphine oxide in water.** C. E. Higgins and W. H. Baldwin (Chem. Div., Oak Ridge National Lab., Tenn., U.S.A.). *Anal. Chem.*, 1960, **32** (2), 236-238.—When centrifuging is performed as part of an analytical procedure, significant temp. rises can occur and consequently solution equilibria are disturbed. It is recommended that air-cooling be used to maintain a constant temp.

K. A. PROCTOR

**4346. Infra-red spectra - structure correlations for organosilicon compounds.** A. Lee Smith (The Dow Corning Corporation, Midland, Mich., U.S.A.). *Spectrochim. Acta*, 1960, **16** (1-2), 87-105.—A comprehensive tabulation of the published i.r. spectra of organosilicon compounds is given together with an absorption wavelength - functional group correlation chart. Identification is helped since the Si atom tends to isolate the groups, so that the compound spectrum is the sum of the component group spectra. Spectra (2 to 16  $\mu$ ) are given for ethyl-, *n*- and *iso*-propyl- and *n*-butyl-trichlorosilanes and tetramethyl and tetraethyl silicates. Solution spectra are given; the spectra of solid or crystalline samples may exhibit shifts in shape or frequency. The commoner aliphatic, aromatic and other groups are treated in detail. R. M. S. HALL

**4347. Gas - liquid chromatographic separation and identification of methylchlorosilanes.** Chung-Chien Yu, Hsieh-Ching Yang, Fu-Ching Su, Chen-Chen Hsien and Ching-Hua Liu (Dept. of Chem., Nankai Univ.). *Acta Chim. Sinica*, 1959, **25** (6), 420-423.—Mixtures of methyltrichlorosilane, dimethyldichlorosilane, trimethylchlorosilane and  $\text{SiCl}_4$  are separated and analysed by the gas - liquid chromatographic technique, benzophenone being used as the stationary phase. The partition column is maintained at 52° in a water jacket. Hydrogen is passed successively through a flow-meter, a thermal control cell and the column. The sample (approx. 0.1 ml) is injected into the hydrogen line between the thermal control cell and the partition column. Chromatograms are recorded as plots of vapour concn., determined by conductivity measurement, against time. A complete analysis takes 80 min.

S. H. YUEN

**4348. Short-term determination of carcinogenic aromatic hydrocarbons.** D. Hoffman and E. L. Wynder (Sloan-Kettering Inst., New York, N.Y., U.S.A.). *Anal. Chem.*, 1960, **32** (2), 295-296.—Polycyclic hydrocarbons, from combustion products and other materials, are enriched by partition between cyclohexane and water. After extraction into nitromethane, the compounds are fractionated by silica gel column chromatography, and finally separated by paper chromatography. By these means, a rapid analysis can be made. An analysis of a cigarette-smoke condensate is described.

G. P. COOK

**4349. Carbon - hydrogen stretching frequencies.** S. E. Wiberley, S. C. Bunce and W. H. Bauer (Dept. of Chem., Rensselaer Polytech. Inst., Troy, N.Y., U.S.A.). *Anal. Chem.*, 1960, **32** (2), 217-221.—A correlation chart of the C-H stretching region for 10 cyclobutyl and 60 aromatic compounds in the region 2700 to 3100  $\text{cm}^{-1}$  is presented and discussed. This information is useful for spectra-structure correlation studies on related materials.

K. A. PROCTOR

**4350. Selective gas - liquid chromatographic separation of aromatic compounds with tetrahalophthalate esters.** S. H. Langer, C. Zahn and G. Pantazoplos (Central Exp. Sta., U.S. Bureau of Mines, Pittsburgh, U.S.A.). *J. Chromatography*, 1960, **3** (2), 154-167 (in English).—By using 7 to 25% w/w of tetrahalophthalic esters as liq. stationary phase, the retention vol. of several aromatic and aliphatic hydrocarbons were measured; aromatics are preferentially retained. The effect of change in the alkoxyl or halogen group of the esters on retention vol. is discussed. Separations of *p*- and *m*-xylenes,

of ethyltoluenes, and of mesitylene and *o*-ethyltoluene have been achieved. The effect of adsorbate structure on separation is discussed with regard to the esters as electron acceptors. Some qualitative evidence for complexing of aromatics with the esters is presented.

P. D. PARR-RICHARD

**4351. Analysis of mixtures of trichlorobenzenes and mixtures of tetrachlorobenzenes by means of their infra-red absorption spectra.** S. B. Bardenshtein, R. V. Dzhangatspanyan and V. I. Zetkin. *Zavod. Lab.*, 1960, **26** (2), 167-171.—Complex mixtures are vacuum-distilled to separate fractions containing trichlorobenzenes from those containing tetrachlorobenzenes, and the infra-red spectra of the separated fractions are obtained. For 1:2:3-, 1:3:5- and 1:2:4-trichlorobenzenes the intensities at 6.97, 11.77 and 8.90  $\mu$ , respectively, are measured, and for 1:2:3:4-, 1:2:4:5- and 1:2:3:5-tetrachlorobenzenes the intensities at 8.50, 7.54 and 11.67  $\mu$  are measured. G. S. SMITH

**4352. Quantitative micro-determination of diphenyl. Quantitative determination of diphenyl in paper wrappers.** A. Rajzman (Dept. of Fruit and Vegetable Storage, Agric. Res. Sta., Rehovot, Israel). *Analyst*, 1960, **85**, 116-121.—The calibration graph is prepared by treating standard soln. of diphenyl in  $\text{CHCl}_3$  with a reagent containing 16.6 mg of formaldehyde per litre in glacial acetic acid and then adding dil.  $\text{H}_2\text{SO}_4$  (2:17) containing a specified small amount of  $\text{Fe}_2(\text{SO}_4)_3$ . The blue colour formed is measured absorptiometrically with an orange filter at 610  $\text{m}\mu$  against the  $\text{H}_2\text{SO}_4$ - $\text{Fe}_2(\text{SO}_4)_3$  reagent. Diphenyl is extracted from impregnated papers with  $\text{CHCl}_3$ , and the extract is purified with bone charcoal. By a specified procedure the vol. required to provide 800  $\mu\text{g}$  of diphenyl is ascertained, this vol. is adjusted to 1 ml, the formaldehyde-acetic acid reagent (9 ml) is added, and the colour is measured absorptiometrically for the calibration. Recovery of added diphenyl is good. The constitution of the blue compound is discussed.

A. O. JONES

**4353. Spectrophotometric estimation of phenol in solutions containing tyrosine, tryptophan, histidine or chymotrypsin.** W. Lee and J. H. Turnbull (Univ. Birmingham, England). *Talanta*, 1960, **3** (4), 318-323 (in English).—Diazoised *p*-nitroaniline (slight excess) is coupled with phenol in phosphate buffer soln. (pH 8) and after 1 min. the soln. is made strongly alkaline. The extinction is measured at 480  $\text{m}\mu$ . Beer's law is obeyed for concn. of phenol from  $1 \times 10^{-5} M$  to  $5 \times 10^{-5} M$ . The reaction with tyrosine, tryptophan and histidine is much slower, and the dinitrodiazaminobenzene formed has an absorption curve (max. at 410  $\text{m}\mu$ ) which is entirely different from that of the phenol complex.

R. M. S. HALL

**4354. New test for the detection of aralkyl and dialkyl ketones containing the -COCH<sub>2</sub>- group.** E. Sawicki, J. Noe and T. W. Stanley (Air Pollution Engng Res., Robert A. Taft San. Engng Center, Cincinnati, Ohio, U.S.A.). *Mikrochim. Acta*, 1960, (2), 286-290 (in English).—*Procedure*—To one drop (0.02 ml) of the test sample in dimethylformamide are added 1 ml of 2:2'-dinitrodiphenyl (1% soln. in dimethylformamide) and one drop of 10% aq. tetraethylammonium hydroxide soln. A blue or violet colour is obtained with an absorption maximum between 560 and 590  $\text{m}\mu$ ; the colour is stable for several minutes. Some compounds that contain

the  $R\text{-CO-CH}_2\text{-}$  group, e.g., diethylaminoacetone, *o*-, *m*- and *p*-hydroxyacetophenone, and ethyl acetoacetate, do not give the colour, neither does 2:4-dimethylpentan-3-one or *trans*-1:4-diphenylbut-2-ene-1:4-dione. Compounds containing active hydrogen, e.g., malononitrile, 1-ethylrhodanine, indane-1:3-dione and octane-2:3-dione, and certain other compounds give a negative reaction. The limits of identification for over 50 ketones are presented.

B. B. BAUMINGER

**4355. New reagent for titrations in anhydrous medium. IV. Determination of salts of organic acids in acetic acid medium with a mixture of chloroaluminium isopropoxide and its hydrochloric acid complex.** I. Simonyi and G. Tokár (Egyesült Gyógyszer- és Tápszergyár Lab., Budapest). *Magyar Kém. Foly.*, 1960, **66** (2), 74-76.—In a mixture of  $\text{CHCl}_3$  (I) and glacial acetic acid (II), chloroaluminium isopropoxide (III) decomposes instantaneously into chloroaluminium acetate (IV) and this reacts with one mole of Na salicylate (V), with the formation of NaCl. The HCl complex of III (for its preparation cf. Tokár and Simonyi, *Ibid.*, 1958, **64**, 379) decomposes in the same solvent mixture to IV and HCl, and these react with two moles of V with the formation of NaCl. *Procedure*—Dry the test material at  $130^\circ$ , then dissolve an aliquot (0.12 to 0.16 g) with slight warming in II (2 ml). To the cold soln. add dry I (20 ml) and a 0.1% soln. of dimethyl yellow in I. Titrate with 0.1 M III or the HCl complex of III. The colour changes from yellow to red. The proportion of I to II must be between 20:1 and 20:3. The same method can be used for the determination of Na benzoate and Na phenylacetate. The probable limit of error is  $\pm 2\%$ .

A. G. PETO

**4356. New method of identification of amines and phenols.** J. Woliński, D. Buza, E. Czerwińska-Fejgin and W. Zamlyński (Dept. of Org. Chem., Polytech., Warsaw). *Chem. Anal., Warsaw*, 1959, **4** (5-6), 989-994.—Benzoylphenyldiazomethane yields crystalline diphenylacetyl derivatives with amines and phenols that have sharply defined m.p. and are suitable for identification. The reaction is carried out at  $60^\circ$  in anhyd. benzene, with a 10% excess of reagent. The reaction is complete when the orange colour is discharged and the evolution of N ceases. The derivatives crystallise when the solvent is distilled off. Melting-points, solvents for re-crystallisation and analytical data are tabulated for the derivatives of 13 amines and 5 phenols.

L. SMAKOWSKI

**4357. Analysis of mixtures of aniline and mono- and di-methylaniline.** Z. E. Zin'kov and L. I. Pylaeva. *Zhur. Anal. Khim.*, 1960, **15** (1), 109-111.—The method involves the determination of the total amount of acid required to neutralise the mixed amines, the amount of nitrite used for diazotising aniline and nitrosating methylaniline and also the amount of acid used to diazotise aniline. From these values it is possible to determine the amount of each amine in the mixture.

A. BURWOOD-SMITH

**4358. Rapid test for identification of the isomers of phenylenediamine.** R. G. Frieser and P. A. Scardaville (Interchemical Corp., New York, N.Y., U.S.A.). *Anal. Chem.*, 1960, **32** (2), 196-197.—Phenylenediamines react with molybdophosphoric acid to form complexes, the colours of which depend on the relative positions of the amino groups in the benzene ring.

G. P. COOK

**4359. The chromatography of polycyclic aromatic hydrocarbons on acetylating paper.** I. T. M.

Spotswood (Univ. Adelaide, Australia). *J. Chromatography*, 1959, **2** (1), 90-94 (in English).—A procedure is given for acetylating paper. The solvent used was ethanol-toluene-water (17:4:1).  $R_F$  values are given for 34 polycyclic hydrocarbons. Some compounds that did not fluoresce were located by spraying with tetrachlorophthalic anhydride [2% in acetone-chlorobenzene (10:1)] and viewing under u.v. light.

II. T. M. Spotswood. *Ibid.*, 1960, **3** (2), 101-110.—A new method for acetylation of paper or cellulose powder gives better results than that described in Part I. Papers with an acetyl content of approx. 21 to 24% give higher  $R_F$  values, but those with 25 to 28% usually give better separations and have been used to determine the position of methyl substitution in derivatives of benzophenanthrene. Non-fluorescing compounds are detected by spraying with tetrachlorophthalic anhydride, fluorescing ones by u.v. light or by a modified photoprint method; spectrophotometry at 250 to 280  $m\mu$  can also be applied. A microsublimation technique for m.p. determination is described. P. D. PARR-RICHARD

**4360. Photometric picric acid method for the determination of naphthalene in its mixtures with phenol.** M. P. Dianov and B. Ya. Teitelbaum. (Chem. Inst. of Kazan, Acad. of Sci., USSR). *Zhur. Anal. Khim.*, 1960, **15** (1), 119-120.—The method is based on the shift to the long-wave region of the absorption band of a  $\approx 0.1$  soln. of picric acid in dichloroethane, in the presence of naphthalene and phenol. The shift for naphthalene is large in comparison with that for phenol, making it possible to determine naphthalene in mixtures with an accuracy up to 1%. *Procedure*—Dissolve the test substance (2 g) in dichloroethane, mix a 5-ml aliquot with an equal vol. of a 4% soln. of picric acid in dichloroethane and measure the extinction against a blank. Calculate the naphthalene concn. from a calibration curve obtained from several phenol-naphthalene mixtures. The first part of the curve (up to 20% by wt. of naphthalene) is approx. linear. It is thus possible to calculate the naphthalene concn. (C) from the formula  $C = 140(E - 0.099)\%$  w/w, 0.099 being the extinction of the phenol picrate soln. K. R. C.

**4361. A paper-chromatographic method for the identification of 1- and 2-naphthols when present together.** M. R. Verma, Ramji Dass and P. K. Gupta (Nat. Phys. Lab., New Delhi, India). *J. Chromatography*, 1960, **3** (2), 197-199 (in English).—1-Naphthol (I) and 2-naphthol (II) are separated by coupling with a diazo compound and chromatographing the dyes obtained. Cold, alkaline diazotised 2-naphthylamine-5:7-disulphonic acid is added to I and II on the paper, and the spots are developed with either (a) isobutyl methyl ketone-ethanol (7:3) saturated with aq.  $\text{NH}_3$  (10%), (b) isoamyl alcohol-ethanol-aq.  $\text{NH}_3$  (8:8:5), or (c) isoamyl alcohol-ethanol- $\text{H}_2\text{O}$  (8:8:5); when (c) is used the paper is treated with 3% NaOH soln. before application of the sample. The  $R_F$  values differ in the three systems, but are separated by 0.14 unit in each case; II always moves faster than I.

P. D. PARR-RICHARD

**4362. Gas chromatography of oxygen-containing terpenes.** G. P. Cartoni and A. Liberti (Inst. Anal. Chem., Univ. of Messina, Italy). *J. Chromatography*, 1960, **3** (2), 121-124 (in English).—Terpenoid esters, alcohols and carbonyl compounds of



b.p. 180° to 240° can be separated and identified by using columns which differ in degree of polarity. With a gas flow-rate of 80 to 100 ml per min. and a column temp. of 132° to 156°, all fractions are eluted in 60 to 100 min. from a 3 to 5-metre column of inactivated Celite containing 20% w/w of either D.C. 550 Silicone oil or of a sucrose derivative (Hyprose SP80). With silicone oil the terpenes are eluted according to their b.p., but with strongly polar Hyprose the functional groups determine the order of elution; retention decreases in the order alcohols, aldehydes or esters, hydrocarbons. With Hyprose, the separation of terpene alcohols is complete.

P. D. PARR-RICHARD

**4363. Photometric titration of camphor in dilute solution by the oxime method.** Masao Noguchi and Masayoshi Kitajima (Central Res. Lab., Japan Monopoly Co-op., Yutaka-cho, Shinagawa-ku, Tokyo). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1959, **80** (11), 1274-1277.—A satisfactory end-point in the titration of excess of hydroxylamine (I) with 0.1 N HCl is obtained by a photometric method with the aid of bromophenol blue (II). An equimolar mixture of I and its hydrochloride is the best pptg. agent for 0.1 to 0.2% of camphor (< 0.1 g) in aq. methanol (15 to 97 g of water per 100 ml). Crude oil of camphor (< 0.1 g) is dissolved in aq. methanol containing 25 g of water per 100 ml, the soln. is boiled under reflux with I soln. (10 ml) for 4 hr., then 0.7 N HCl (10 ml) is added and the soln. is titrated at 587 m $\mu$  with 0.1 N HCl, with II as indicator. The I soln. is prepared by treating 6-8 g of I hydrochloride in 10 ml of water with KOH (2.5 g) in methanol, diluting to 50 ml with methanol and filtering off the KCl. Camphor-tree leaves (10 g) are steam-distilled with 300 ml of water for 1 hr., the distillate is diluted to 100 ml with methanol, and similarly titrated.

K. SAITO

**4364. Gas-chromatographic determination of camphor.** Yoshio Hanada and Masayoshi Kitajima (Central Res. Lab., Japan Monopoly Co-op., Yutaka-cho, Shinagawa-ku, Tokyo). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1959, **80** (11), 1272-1274.—Gas chromatography of crude camphor (carrier gas, He; column diameter, 6 mm; length, 3.75 metres) was examined with reference to the use of an internal standard. Since the difference in  $R_T$  values for camphor (I) and naphthalene (II) is sufficiently large (0.79:1) for both peaks to be separated at 190° at a rate of 60 ml per min., II is used as standard. I (7 to 90%) in cineole,  $\alpha$ -pinene, safrole or dipentene is determined with an error of  $\pm 1\%$ .

K. SAITO

**4365. Gas-liquid chromatography of pyridines using a new solid support.** A. W. Decora and G. U. Dinneen (Bureau of Mines, U.S. Dept. Interior, Laramie, Wyo., U.S.A.). *Anal. Chem.*, 1960, **32** (2), 164-169.—The support was prepared from a commercial detergent (Tide) by heating it and then extracting it with light petroleum. The porous material remaining after extraction was used as the solid support. When used in conjunction with non-polar substrates, symmetrical peaks were obtained for pyridines, and a complete separation of a test mixture containing 14 of them was attained. Retention data for 15 pyridines on various liquid substrates are listed.

G. P. COOK

**4366. Aminolysis of epoxides. V. Determination of pyridine derivatives with epoxides.** H. J. Roth and H. O. Schrimpf (Inst. f. Pharm. u. Lebens-

mittelchem., Univ., Würzburg, Germany). *Arch. Pharm., Berlin*, 1960, **293** (2); *Mitt. dtsh. pharm. Ges.*, 1960, **30** (2), 22-28.—To determine isoniazid, dissolve the sample ( $\approx 4$  mg) in methanol (1 ml), add a soln. of 1-chloro-2:3-epoxypropane (50 mg) in methanol (1 ml), heat at 70° for 2 hr., cool, add a 20% soln. of Na methoxide (one drop), dilute to 10 ml with methanol, set aside for 30 min. and measure the extinction at 465 m $\mu$ . To determine 1-isonicotinoyl-2-isopropylhydrazine phosphate, follow a similar procedure, but first render the sample alkaline by addition of methanolic KOH. Similar methods are used for the determination of nicotinamide, nikethamide, quinine, cinchonidine, papaverine and bisacodyl, but styrene oxide is used in place of 1-chloro-2:3-epoxypropane.

A. R. ROGERS

**4367. Nuclear magnetic resonance of pyridine derivatives.** M. Freymann, R. Freymann and D. Libermann. *Compt. Rend.*, 1960, **250** (12), 2185-2187.—The nuclear magnetic resonance spectra of 2-aminotriazine, 2-, 3- and 4-methylpyridines, 2-, 3- and 4-cyanopyridines, 2-aminopyridine, quinoline, 2:2'-dipyridyl and nicotine are reported, and the  $\delta$  and J effects of the  $\alpha$ ,  $\beta$  and  $\gamma$  lines of the protons are specified. Observed line displacements are ascribed to the differing induction and mesomeric effects of NH<sub>2</sub>, CH<sub>3</sub> or CN groups.

W. J. BAKER

**4368. Investigation of anomalous reactions in the amino-nitrogen determination. IX. The reaction of pyrroline and oxazoline compounds with nitrous acid.** G. Kainz and H. Huber (II Chem. Inst., Univ. Wien). *Mikrochim. Acta*, 1960, (2), 245-253 (in German).—Pyrroline and oxazoline compounds react with HNO<sub>2</sub> and evolve 1 mole of N at 20°; pyrroline compounds give 1.40 moles of a mixture of N and N<sub>2</sub>O at 80°. It is claimed that NOBr in glacial acetic acid (cf. *Mikrochim. Acta*, 1959, 51) gives quant. results, whereas the usual Van Slyke method with aq. nitrite soln. gives incorrect results. [No analytical procedure is given.]

H. M.

**4369. Rapid decomposition and analysis procedure for micro-determination of chlorine compounds in petroleum fractions.** H. V. Malmstadt and J. D. Winefordner (Univ. Ill., Urbana, U.S.A.). *Anal. Chem.*, 1960, **32** (2), 281-284.—The decomposition apparatus is based on the combustion of the sample in an oxy-hydrogen flame with a system open to the atmosphere. The products of combustion are condensed and collected in a soln. of H<sub>2</sub>SO<sub>4</sub>. The Cl<sup>-</sup> are then titrated potentiometrically with the null-point method. Samples containing 1 to 10 p.p.m. of Cl can be determined with a standard deviation of about 0.1 p.p.m., and relative errors are about 1% for samples containing  $\approx 100$  p.p.m. of Cl.

G. P. COOK

**4370. Determination of traces of vanadium, iron and nickel in petroleum oils by X-ray emission spectroscopy.** Chia-Chen Chu Kang, E. W. Keel and E. Solomon (Res. and Devel. Lab., The M. W. Kellogg Co., Jersey City, U.S.A.). *Anal. Chem.*, 1960, **32** (2), 221-225.—The method described is rapid and direct and all three elements can be determined in about 40 min. with an estimated accuracy of  $\pm 1$  p.p.m. or  $\pm 5\%$  of the amount present, whichever is greater. Correction has to be made for absorption due to S, but the effect of other elements is negligible.

K. A. PROCTOR

**4371. The determination of sulphur trioxide and sulphur dioxide in flue gases.** R. S. Fielder, P. J. Jackson and E. Raask (Central Electricity Res. Lab., Leatherhead, Surrey). *J. Inst. Fuel*, 1960, **33**, 84-89.—A portable apparatus is described with which determinations of  $\text{SO}_2$  and  $\text{SO}_3$  in flue gas can be made at the rate of one every 20 min. The gas is drawn by a diaphragm pump through an uncooled sampling probe and a filter and is saturated with cold aq. isopropyl alcohol. The mist of  $\text{H}_2\text{SO}_4$  is collected on a filter and determined as  $\text{BaSO}_4$ , either turbidimetrically or by titration. The  $\text{SO}_2$  is determined by the vol. of sample required to decolorise a known amount of standard iodine soln. A rotameter is used to measure the gas flow.

G. BURGER

**4372. Determination of carbon and hydrogen in solid fuels.** W. Radmacher and A. Hoverath (BrennstChem. Inst., Ruhrkohlen-Beratung G.m.b.H., Essen, Germany). *BrennstChemie*, 1960, **41** (2), 52-54.—The Sheffield high-temp. method (*cf. Fuel, London*, 1957, **36**, 39) has been simplified. The sample (60 mg) is burned at  $1050^\circ$  in oxygen (50 ml per min.) in a quartz tube without packing save in its final third, which contains silver wool at  $640^\circ$  to retain halogens and S. After 150 analyses the silver may need regeneration by passing through it a current of H. Special absorption vessels contain enough  $\text{Mg}(\text{ClO}_4)_2$  and NaOH-asbestos for  $\approx 40$  analyses. A determination takes 25 min. Duplicate tests on coke, coal and brown coal had a standard deviation of  $\pm 0.11\%$  for C and  $\pm 0.05\%$  for H; agreement with results by the German official method (DIN 51721/4.1) was satisfactory.

A. R. PEARSON

**4373. New apparatus for radiometric determination of the ash content of coal by means of the absorption of  $\gamma$ -radiation.** R. Jirkovský (Vysoká Škola Báňská, Ostrava, Czechoslovakia). *Jaderná Energie*, 1960, **6** (2), 63-64.—An integrator was used for the measurement of the absorption of  $\gamma$ -radiation and a Geiger-Müller tube or a photomultiplier with a crystal as the detector. The measurement is carried out by the comparison of the sample with a standard of a pure coal (ashless) or of a sample of coal with a known ash content. The whole procedure can be completed within 6 min. with an accuracy within  $\pm 0.4\%$ .

J. ŽYKA

**4374. Oxidation of coal. II. Determination of benzenepolycarboxylic acids.** J. E. Germain and F. Valadon (Centr. de Carbochimie, 3<sup>e</sup> Cycle, Fac. des Sci. de Lille, France). *Bull. Soc. Chim. France*, 1960, (1), 11-16.—Separation of benzenepolycarboxylic acids by partition chromatography on a column is investigated and a suitable column described. *Procedure*—The column is prepared by washing a Celite (Johns Manville lot 525) with 0.1 N HCl and then water and drying, mixing this with an equal vol. of crushed glass (30 to 24 AFNOR mesh), and placing the mixture in a column (200 mm  $\times$  18 mm). The samples, added to the column as ammoniacal soln., are adsorbed on the Celite, then the column is eluted, under N pressure, successively with ethanol and ethanol containing an increasing proportion of water (6%, 12%, 17%, 25%, 40% and 55%), each eluent containing 3% of KOH. The polycarboxylic acids are determined in the fractions collected by their extinctions at 230 m $\mu$ . The method is used for the determination of the benzenepolycarboxylic acids produced by the oxidation of coal.

E. J. H. BIRCH

**4375. Detection of oxidised starches.** J. R. Fraser and D. C. Holmes (D.S.I.R., Lab. of the Gov. Chemist, Clement's Inn Passage, Strand, London). *Analyst*, 1960, **85**, 150-151.—Oxidised starch has a greater dye-absorbing power than unmodified starch. The sample (0.5 g) with 10 ml of a 0.1% aq. soln. of safranin and water to  $\approx 190$  ml is swirled frequently during 1 hr. and then the mixture is diluted to 200 ml. The liquid is centrifuged, 10 ml of the clear supernatant liquid is diluted to 50 ml, and the reduction of colour is measured by comparison with standard soln. of safranin, visually or by means of a comparator or, preferably, spectrophotometrically at 515 to 520 m $\mu$ . Certain other dyes may be used with suitable alterations in the dilutions and the absorption wavelength. Typical results for maize and potato starches are quoted.

A. O. JONES

**4376. New method for conductimetric titration of surface-active agents such as alkylarylsulphonates, alkylsulphonates and alkyl sulphates with p-toluidine hydrochloride.** H. Niewiadomski, W. Zwierzykowski and M. Płoszyński (Dept. of Technol. of Fats, Polytech., Danzig). *Chem. Anal., Warsaw*, 1959, **4** (5-6), 995-997.—The method of Stüpel and Segesser (*Brit. Abstr. C*, 1952, 56) and Wickbold (*Fette, Seif., Anstrichmitt.*, 1955, **57**, 164) was simplified to permit the direct titration of the surface-active agent with 0.1 N or N aq. p-toluidine hydrochloride. The sample (1 to 4 g) was dissolved in water (50 ml) and the titration was carried out with constant stirring, the end-point being at the point of minimum conductivity; the time required was 5 to 15 min. Results are quoted for 5 compounds.

L. SMAKOWSKI

**4377. Alternating current polarography of [surface-active] organic compounds and the influence of solvents.** K. Schwabe and H. Jehring (Inst. f. Elektrochem. u. phys. Chem., Tech. Hochschule, Dresden, Germany). *Z. anal. Chem.*, 1960, **173** (1), 36-43 (in German). The polarographic method of Breyer (*Öst. ChemZtg*, 1956, **57**, 67) in which a small a.c. voltage is superimposed on the applied d.c. voltage and only the a.c. current recorded has been applied to the study of surface-active organic compounds. It is shown that, on introducing organic solvents into the basal soln., a decrease in height of the recorded maxima is associated with a shift of  $E_1$  to more negative potentials.

T. R. ANDREW

**4378. Analytical studies of surface-active agents. IV. Differentiation between polyoxyethylene glycol and polyoxypropylene glycol.** C. J. Turi and G. De Guili (Lab. Chim., Ist. Sup. di Sanit., Roma, Italy). *R.C. Ist. Sup. Sanit.*, 1960, **23** (2), 140-145.—Polyoxyethylene and polyoxypropylene glycols are differentiated and identified by pyrolysis and identification of their degradation products (acetaldehyde and propionaldehyde, respectively) by means of the formation of their 2:4-dinitrophenylhydrazones. The derivatives were identified by paper chromatography (mobile phase, hexane saturated with methanol; stationary phase, methanol saturated with hexane) and by their i.r. spectra.

E. C. APLING

**4379. Oxidimetric determination of dyes.** M. Matrká (Res. Inst. Org. Synth., Pardubice-Rybitví, Czechoslovakia). *Chem. Listy*, 1960, **54** (3), 219-223.—A survey is presented of titrations with  $\text{KMnO}_4$ ,  $\text{Ce}(\text{SO}_4)_2$ ,  $\text{K}_2\text{Cr}_2\text{O}_7$  and  $\text{Fe}_2(\text{SO}_4)_3$  (11 references).

J. ŽYKA

**4380. Cleanliness of fillings and stuffings for bedding, upholstery, toys and other domestic articles.** British Standards Institution (2 Park Street, London, W.1). B.S. 1425:1960. 62 pp.—

Methods are given in appendices for sampling, and cleanliness, and for the determination of dry matter, oil and soap, animal-fibre content, trash, chlorine as soluble chlorides, dust index, cotton-kapok mixtures, cotton-man-made fibre mixtures, man-made fibres, dross content of feathers and down, down in mixtures with poly(vinyl cyanide) fibres, and acetone-insol. matter in bonded secondary cellulose acetate fibres.

**4381. Quantitative determination of artificial protein fibres in yarn blends.** E. Frieser. *Textilrdsch.*, 1960, **15** (2), 65-72.—A survey of the possibilities for the qual. differentiation between artificial protein fibres [ninhydrin reaction, Morse test, swelling in conc.  $H_2SO_4$ , solubility in  $N HCl$ , dyeing with Alizarin red AS (C.I. Mordant Red 3), determination of phosphate content] is made and methods for the quant. determination of regenerated protein fibres (from milk casein, maize zein, soya and ground-nut protein) in the presence of wool, cotton and viscose-rayon staple fibres are discussed in detail. The methods described are applicable only to rovings, yarns and knitted and woven fabrics. For the quant. analysis of felt, special measures are necessary for dissolution.

BRIT. COTT. IND. RES. ASS. ABSTR.

**4382. Methods of testing plastics. Part 5: Miscellaneous methods.** British Standards Institution (2 Park Street, London, W.1). B.S. 2782: Part 5: 1958. Amendment No. 3 (10.3.60).—Several corrigenda are listed.

**4383. Application of the oxygen flask combustion method to the determination of chlorine in polymers, plasticisers and organic compounds.** J. Haslam, J. B. Hamilton and D. C. M. Squirrell (I.C.I. Ltd., Plastics Div., Welwyn Garden City, England). *J. Appl. Chem.*, 1960, **10** (2), 97-100.—*Procedure*—The sample (containing 5 to 6 mg of Cl) is wrapped in Whatman No. 42 filter-paper and inserted in an 80-mesh platinum-gauze basket attached to the stopper of a 500-ml separating-funnel. The funnel is charged with 1 ml of  $N NaOH$ , 3 ml of water and 3 drops of 35%  $NaHSO_3$  soln. (to decompose oxides of Cl) and filled with  $O_2$ . The paper is ignited and the stopper and basket are inserted in the funnel, which is inverted so that the absorption soln. seals the stopper. After complete combustion the funnel is shaken and after 5 to 10 min. the contents are run into a 50-ml beaker. The funnel, stopper and basket are washed till the total vol. of soln. is 30 to 35 ml. The excess of  $NaHSO_3$  is destroyed with 6 drops of 100-vol.  $H_2O_2$  and the soln. is neutralised to methyl red with  $N HNO_3$  and 0.15 ml in excess is added. The soln. is then titrated with 0.01  $N AgNO_3$  in an automatic titrimeter (Haslam and Squirrell, *Anal. Abstr.*, 1959, **6**, 4644). Blank and calibration determinations are carried out. It is probable that the method is equally applicable to the determination of Br.

E. J. H. BIRCH

**4384. Rapid method for the determination of chlorine in high polymers.** J. Fertig. *J. Appl. Polymer Sci.*, 1959, **2** (4), 125.—By applying the Schöniger combustion method (*Anal. Abstr.*, 1955, **2**, 1816; 1957, **4**, 924) in place of conventional methods, the total time for the analysis is shortened to 20 to 35 min. Results are between 94 and 99%

of the theoretical values, varying with the polymer analysed. REV. CURR. LIT. PAINT COL. VARN.

**4385. Use of ion-exchange resins in plastics analysis.** E. Schröder (Inst. f. Chem. u. Technol. d. Plaste, Leipzig, Germany). *Plaste u. Kautsch.*, 1959, **6** (7), 325-326.—Methods for the identification of cellulose esters, polyvinyl esters, and various types of polyamides, involving hydrolysis, treatment with suitable ion-exchange resins, and identification of the acid component liberated, are described.

L. A. O'NEILL

**4386. Determination of degree of unsaturation of unsaturated polyesters.** K. M. Gréger, I. V. Szmeccsányi and E. M. Bödi. *Magyar Kém. Lapja*, 1960, **15** (2), 72-74.—The polyesters are hydrolysed with aq.  $NaOH$  soln. and the unsaturated components, maleic and fumaric acid, are oxidised with  $BrCl$ . *Procedure*—Dissolve a weighed sample of polyester resin (0.5 to 1 g) in acetone (10 ml). Add 0.5  $N NaOH$  until a 20% excess is present and after shaking for 1 hr. neutralise the excess with 0.5  $N HCl$ . Evaporate to dryness, dissolve the residue in water and dilute to 100 ml. To samples (10 ml) of this soln. add 0.1  $N KBrO_3$  (20 ml) and 20%  $HCl$  (10 ml) and, after 6 hr.,  $KI$  (1 to 2 g); titrate with 0.1  $N Na_2S_2O_3$ , with starch as indicator.

G. SZABO

**4387. Determination of copolymer composition by combustion analysis for carbon and hydrogen.** L. A. Wood, I. Madorsky and R. A. Paulson (Nat. Bur. of Standards, Washington, D.C., U.S.A.). *J. Res. Nat. Bur. Stand., A*, 1960, **64** (2), 157-162.—The apparatus and procedure described permit the determination of the C to H ratio in a copolymer and hence of its composition, as for example, the content of bound styrene in a styrene-butadiene copolymer used as a reference standard in developing new procedures or for studying the variation of specific properties (such as refractive index) with composition. The combustion apparatus is a modification of that used by Wagman and Rossini (*J. Res. Nat. Bur. Stand., A*, 1944, **32**, 44). Minor constituents (soap, fatty acids, stabiliser, low-mol.-wt. polymer) must be removed initially by extraction or otherwise, but the bound thiol residue should be determined from measurements of the content of S by the Carius method, and the necessary correction applied when calculating the ratio of C to H. The standard deviation is  $\approx 0.001$  (6 analyses) and is independent of the content of styrene; expressed as bound styrene, the standard deviation is 0.036% for low-styrene polymers and 0.018% for high-styrene ones.

W. J. BAKER

**4388. Determination of nitrogen content of acrylic polymers. II.** Suez Kishimoto (Toyo Rayon Co., Otsu, Shiga-ken). *Japan Analyst*, 1959, **8** (9), 599-600.—The nitrogen content of vinyl cyanide-methylvinylpyridine copolymer (I) is satisfactorily determined by the Dumas method, the sample being covered with  $CuO$  in the boat. I is also satisfactorily decomposed by the conc. phosphoric acid method (cf. Takayama and Kadota, *Anal. Abstr.*, 1960, **7**, 623).

K. SAITO

**4389. New colour reaction for methacrylate monomer and polymer identification.** E. B. Mano (Inst. Nac. de Tecnol., Rio de Janeiro, Brazil). *Anal. Chem.*, 1960, **32** (2), 291.—The sample is depolymerised and then heated with conc.  $HNO_3$ . The resulting yellow soln. is cooled, and  $H_2O$  and zinc powder are added. A blue colour develops

immediately if methacrylate resins are present. The colour can be extracted with  $\text{CHCl}_3$  and is also formed if  $\text{NaNO}_2$  is used instead of zinc powder.

G. P. COOK

**4390. Assay of  $\epsilon$ -caprolactam.** L. Márkus and A. Kayser. *Magyar Kém. Lapja*, 1960, **15** (2), 86.— $\epsilon$ -Caprolactam can be hydrolysed by HCl to hexanoic acid and then titrated potentiometrically. *Procedure*—Adjust a sample (20 to 30 ml), containing 0.3 to 1.0 g of  $\epsilon$ -caprolactam, with HCl to approx.  $N$  concn. Heat under reflux for 4 hr., cool and titrate potentiometrically by adding  $N$  NaOH in 0.25-ml portions. The difference between the two observed neutralisation points is equivalent to the  $\epsilon$ -caprolactam. The method can be applied for assaying crude lactams, in the presence of  $(\text{NH}_4)_2\text{SO}_4$ , oximes and tarry impurities, and for polymer products. The coeff. of variation is  $\pm 0.5\%$ , and the maximum deviation  $\pm 1\%$ .

G. SZABO

**4391. Determination of epoxy-group content in epoxy resins by infra-red spectrophotometry.** A. Snowacka (Dept. of Tech. Physics, Inst. of Gen. Chem., Warsaw). *Chem. Anal., Warsaw*, 1959, **4** (5-6), 959-969.—Two procedures for the determination of epoxy groups in non-hardened epoxy resins were developed. (i)—The epoxy-group content was evaluated from a calibration curve prepared by means of standard soln. of constant concn. (2 g per 10 ml) prepared from different resins previously analysed by chemical methods. These gave a linear plot indicating that the absorption per epoxy group in standard resins is constant. (ii)—Soln. of different concn. of the same resin, of high epoxy-group content (0.62 epoxy group per 100 g) and low viscosity, were used as standards. The calibration curve was linear in this case also. The results for three epoxy resins are tabulated and absorption curves are given.

L. SMAKOWSKI

**4392. Application of ion-exchange methods to wax analysis.** W. Presting and S. Jänicke (Inst. f. Verfahrenstechn. org. Chem., Leipzig, E. Germany). *Fette, Seif., Anstrichmitt.*, 1960, **62** (2), 81-87.—The wax is dissolved in boiling benzene (I) and the soln. is passed down a jacketed column of a strongly acid cation-exchanger (Wofatit KPS 200, a polystyrenesulphonic acid resin), heated to  $65^\circ$ , to separate the cations. The resin is washed with isopropyl alcohol and the soln. are evaporated. The residue can be used for column or anion-exchange chromatography. The cations can be recovered by eluting with ethanol. The anion exchange is carried out on Wofatit SB or Wofatit SBS-400 (a polyvinylbenzylammonium resin, similar to Amberlite IRA or Dowex 2). The solvent and temp. are the same as before, except that the column is washed with I. The anions can be eluted with 8  $N$  acetic acid in isopropyl alcohol-I (1:1) at  $65^\circ$ . The saponifiable constituents of the wax can be determined as follows. The wax, dissolved in I, is hydrolysed with 0.5  $N$  alcoholic KOH and then acidified with HCl. The soln. is washed free from  $\text{Cl}^-$  with water and then passed through the anion-exchange column. The acids can be recovered from the column as already described.

A. G. PETO

**4393. Saponification cloud test for beeswax.** H. R. Parker (The Candle Manufacturers Ass., New York). *Drug Standards*, 1960, **28** (1), 26-29.—Heat the sample (3 g) under reflux for 2 hr. with 0.5  $N$  ethanolic KOH, immerse in a bath of water at  $80^\circ$  and allow bath and flask to cool with rotation

of the flask. The soln. should show no cloudiness or globule formation at temp.  $> 65^\circ$ . Hydrocarbons and glycerides of natural origin increase the cloud-point, but carnauba wax and glycerides of artificial origin cannot be detected by this method.

A. R. ROGERS

See also Abstracts—4110, Impurities in acetic acid. 4200, Titanium in organosilicon comp. 4412, Chromatographic detection of carbohydrates. 4487, Detection of quaternary ammonium comp. 4511, Xylene in air. 4532, Chromatography of 3-amino-1:2:4-triazole. 4541, Micro-balance for fibres. 4542, Weighing tube for volatile liquids. 4589, Analysis by critical miscibility temp.

#### 4.—BIOCHEMISTRY

##### INCLUDING DRUGS, FOOD, SANITATION, AGRICULTURE

##### Biological fluids, animal and vegetable tissues

**4394. Determination of water in serum.** P. Paaby (Central Lab., Aalborg County Hospital, Denmark). *Scand. J. Clin. Lab. Invest.*, 1959, **11** (2), 117-121.—Two methods are described and compared, viz, vacuum drying at  $70^\circ$  for 16 hr. and the Karl Fischer titrimetric method. In the first method, aliquots (0.5 ml) of serum are weighed into dry stoppered weighing-bottles, and are placed in a cold vacuum oven; the stoppers are removed, and the temp. is gradually raised to  $70^\circ$  whilst a vacuum of 23 torr is applied. After drying the samples for 16 hr., the stoppers are replaced and the bottles are placed in a desiccator for 30 min. before re-weighing. At constant temp., pressure, and drying time, reproducible results are obtained. It is concluded that this method is simple, very accurate and cheap, whereas the Karl Fischer method is more rapid, but is technically difficult, less accurate and more expensive, and gives results which are consistently 0.2 to 0.3% greater than those by the drying method.

D. B. PALMER

**4395. Spectrophotometric measurement of oxygen saturation of blood in the determination of cardiac output. A comparison with the Van Slyke method.** A. Holmgren and B. Pernow (Karolinska Sjukhuset, Stockholm, Sweden). *Scand. J. Clin. Lab. Invest.*, 1959, **11** (2), 143-148.—The spectrophotometric method of Drabkin and Schmidt (*J. Biol. Chem.*, 1945, **157**, 69) as modified by Nahas (*Amer. J. Physiol.*, 1950, **163**, 737) is shown to give higher values than the manometric method of Van Slyke. This difference is ascribed to the presence in human blood of 3% of inactive haemoglobin. The errors of both methods are found to be of the same order, and of similar magnitude to those reported by other workers. It is further shown that either method is suitable for the determination of the O difference of arterial and venous blood according to the Fick principle. The spectrophotometric method has the advantage of requiring smaller volumes of blood, and is thus more suitable for serial determinations.

D. B. PALMER

**4396. Direct titration of calcium in urine with EDTA.** O. P. Foss (Norwegian Radium Hospital, Oslo). *Scand. J. Clin. Lab. Invest.*, 1959, **11** (2), 211-212.—Urine (diluted 1:1, 6 ml) is adjusted to



pH < 6.0, and passed through a column (10 cm × 9 mm) of Dowex 1-X (200 to 400 mesh) under pressure. This treatment removes phosphates, which interfere with the determination. The first 4 ml of the percolate is discarded, and the calcium content of the next 1 ml is determined by the method of Schwarzenbach *et al.* (*Helv. Chim. Acta*, 1946, **29**, 811), with the apparatus of Foss and Andersen (*Scand. J. Clin. Lab. Invest.*, 1958, **10**, 437). This method gives results which agree favourably with those obtained by the oxalate pptn. method of Wang (*J. Biol. Chem.*, 1935, **111**, 443), and recoveries of 98% to 99% are reported.

D. B. PALMER

**4397. Direct stepwise photo-electric EDTA titration of calcium and magnesium in serum, cerebrospinal fluid and urine.** L. R. Gjessing (Central Lab., Ullevål Hospital, Oslo, Norway). *Scand. J. Clin. Lab. Invest.*, 1959, **11** (2), 190-193.—The sample (0.1 ml) is added to a mixture of 1.5 ml of 0.3 N NaOH and 0.025 ml of 0.1% aq. murexide soln. The mixture is placed in an EEL automatic titrator and EDTA (disodium salt) soln. (1 milli-equiv. per litre) is slowly added until the extinction begins to decrease. This is the end-point for the calcium determination. The soln. is then removed from the titrator, 0.9 ml of 0.6 N glycine is added, and the mixture is boiled for 20 min. to destroy murexide; 0.05 ml of Eriochrome black T soln. is then added and the titration is continued until the end-point is again reached. This gives the magnesium content. Reagent blanks are obtained by the method of double titration of standard soln. (5 milli-equiv. per litre) of Ca and Mg. Recoveries are 99 to 103%. The method is simple and rapid.

D. B. PALMER

**4398. The spectrochemical determination of total strontium in bone, milk and vegetation.** R. V. Jury, M. S. W. Webb and R. J. Webb (A.E.R.E., Woolwich Outstation, London). *Anal. Chim. Acta*, 1960, **22** (2), 145-152.—Samples of bone ash are pelleted with anhydrous copper sulphate and graphite for excitation in a d.c. arc. The spectra are evaluated by microphotometry at 4704-6 Å. The method is effective over the range 50 to 350 p.p.m. of Sr in the ash, and the coeff. of variation for single exposures is 6% at the 90 p.p.m. level. The calcium-strontium fraction has to be taken from samples of milk and vegetation by precipitation as oxalate before using this method, or a flame-photometric method, also described, may be applied.

E. G. CUMMINS

**4399. Determination of radioactive strontium in urine.** V. Zboril, I. Šebastian, T. Trnovec and K. Durček (Inst. Hyg. and Ind. Diseases, Bratislava, Czechoslovakia). *Chem. Zvesti*, 1960, **14** (2), 91-94.—*Procedure*—To 1.5 litres of urine add a known amount of  $^{89}\text{SrCl}_2$  in 0.8 N HCl. Then add Ba (20 mg) and Sr (30 mg) as carriers, mix, and add a satd. soln. of  $\text{Na}_2\text{CO}_3$  (15 ml) and conc. aq.  $\text{NH}_3$  (10 ml). Set aside for 12 hr. Separate the ppt. in a centrifuge, dissolve it in a small vol. of 65%  $\text{HNO}_3$  and dilute with  $\text{H}_2\text{O}$  to 4 ml. Add, with stirring, conc.  $\text{HNO}_3$  (6 ml), cool, separate the pptd. nitrates of Ba and Sr by centrifuging and repeat the procedure. Dissolve the ppt. in  $\text{H}_2\text{O}$  (10 ml), add 2%  $\text{FeCl}_3$  soln. (1 ml) and conc. aq.  $\text{NH}_3$ . Separate the  $\text{Fe}(\text{OH})_3$  by centrifuging. Neutralise the soln. with conc. HCl to phenolphthalein, add 6 M oxalic acid (1 ml), 6 M ammonium acetate (2 ml) and 5%  $\text{Na}_2\text{CrO}_4$  soln. (1 ml). After 30 min. separate the  $\text{BaCrO}_4$  by centrifuging. Add 20%

NaOH soln. (3 ml) and satd.  $\text{Na}_2\text{CO}_3$  soln. (2 ml), then separate the  $\text{SrCO}_3$  by centrifuging; dissolve the ppt. in a few drops of conc. HCl, dilute with  $\text{H}_2\text{O}$  and repeat the procedure. Wash the ppt. thrice with  $\text{H}_2\text{O}$ , transfer to aluminium plates and evaporate to dryness. Weigh, and measure the activity. Compare with standards containing in 10 ml the same amount of  $^{89}\text{Sr}$  and treated by the procedure described above.

J. ZÝKA

**4400. Determination of zinc and copper in biological matter.** K. O. Råker (Agrikulturchem. Inst. Justus-Liebig Univ., Giessen, Germany). *Z. anal. Chem.*, 1960, **173** (1), 57-58 (in German).—Sufficient of the sample to contain 1 to 10 µg of Cu and 10 to 100 µg of Zn is taken and digested with  $\text{HNO}_3$ - $\text{HClO}_4$ . Copper is extracted into  $\text{CHCl}_3$  with dithione at pH 1, while Zn is similarly extracted from a soln. buffered to pH 5 (with citrate and acetate). The combined extracts are evaporated to dryness and organic matter is destroyed by fuming with  $\text{HClO}_4$  and  $\text{H}_2\text{SO}_4$ . The residue is dissolved in an alkaline phthalate basal soln. and the polarogram is recorded in the usual manner. The procedure has been applied to soil extracts, plant substances and stable manure.

T. R. ANDREW

**4401. Histochemical test for cerium in tissues.** J. Fischer, V. Fischerová-Bergerová and E. Vašáková (Inst. Hyg. and Ind. Diseases, Prague). *Pracovní Lékařství*, 1960, **12** (1), 26-27.—The blue complex of  $\text{Ce}^{3+}$  with the indicator bromopyrogallol red at pH 7.2 was used for the detection of Ce in tissues (> 1 mg of Ce per 1 g of sample). Copper interferes, but can be distinguished by the reaction with sulphide.

J. ZÝKA

**4402. Methods of lead determination in urine.** G. Machata and H. Neuninger (Inst. gerichtliche Med., Univ. Wien, Austria). *Wien. Med. Wochschr.*, 1960, **110** (2), 39-41.—After a discussion of spectrographic and polarographic methods, a colorimetric dithione procedure is described for the determination of total Pb. The sample (100 to 200 µl) is evaporated with HCl (1:2) (5 ml) and ashed at 500° to 550°. The ash is dissolved in 20%  $\text{HNO}_3$  soln. (5 to 10 ml), and treated with satd. aq. Na citrate soln. (25 ml) and thymol blue, followed by conc. aq.  $\text{NH}_3$  to the colour change from red to yellow (pH ≈ 2). Thallium, Bi and Zn are then extracted with 0.03% dithione in  $\text{CCl}_4$ , and the aq. phase is treated with aq.  $\text{NH}_3$  to the colour change from yellow to blue (pH ≈ 8.8). If a gelatinous ppt. forms, more citrate soln. is added. Potassium cyanide soln. (5%) (5 ml) and hydroxyammonium chloride soln. (10%) (5 ml) are added, and the Pb is extracted with dithione soln. in  $\text{CCl}_4$ , and determined at 620 mµ in the usual manner.

S. BAAR

**4403. Fluorimetric micro-determination of selenium in biological material.** F. B. Cousins (Med. Sch., Univ. Otago, Dunedin, New Zealand). *Aust. J. Exp. Biol. Med. Sci.*, 1960, **38** (1), 11-15.—The biological material is wet-ashed in 70%  $\text{HClO}_4$ - $\text{HNO}_3$  (sp. gr. 1.42) (1:3). Selenium is co-pptd. with As (Luke, *Anal. Abstr.*, 1959, **6**, 4370) and finally complexed with 3:3'-diaminobenzidine (I) according to the method of Cheng (*Anal. Abstr.*, 1957, **4**, 1189). The Se-I complex is extracted into toluene, and for Se contents of 2 to 50 µg the absorption at 420 mµ is measured or, when the content of Se is < 4 µg, the fluorescence is measured at 580 mµ after excitation at 450 mµ.

G. P. MITCHELL

**4404. Improvements in or relating to test tablets.** H. Lloyd & Co., Ltd. [Inventor: H. A. Fisher]. Brit. Pat. 831,894; date appl. 6.5.57.—In test tablets for analyses which have to be carried out away from laboratory facilities and in which the analytical reagent requires the presence of an acid for their action, the acid employed is furoic acid. The test tablets may also contain a solid disintegrating agent, e.g., alginic acid. A Griess reagent in tablet form for testing for nitrite in urine contains, e.g., 1-naphthylamine hydrochloride 15.3%, sulphonic acid 1.8%, furoic acid 72.9% and alginic acid 10.0%.  
J. M. JACOBS

**4405. Separation and identification of caffeine, phenazone and phenacetin from human tissue.** R. Bonnichen, A. C. Maehly and S. Nordlander (Gov. Lab. for Forensic Chem., Stockholm, Sweden). *J. Chromatography*, 1960, **3** (2), 190-192 (in English).—After extraction of acidified tissue with  $\text{CHCl}_3$  and removal of fat and strongly acid material, caffeine (I), phenazone (II) and phenacetin (III) together with barbiturates are separated by descending chromatography on paper treated with 0.05 M  $\text{Na}_2\text{CO}_3$  with diethyl ether as the mobile phase.  $R_F$  values for I, II and III are 0.41, 0.55 and 0.90, but certain barbiturates have similar values in this system. The spots are located by placing the chromatogram over a paper treated with weak ammoniacal fluorescein soln. and irradiating with u.v. light. The eluted materials are identified by their u.v. and i.r. spectra and by their m.p.  
P. D. PARR-RICHARD

**4406. Improved method for the isolation and estimation of furan-2:5-dicarboxylic acid in human urine.** B. Flaschenträger and S. M. A. Wahhab (Biochem. Dept., Fac. of Med., Alexandria Univ., U.A.R.). *Mikrochim. Acta*, 1960, (2), 275-281 (in English).—The extraction apparatus described and illustrated is a modification of that constructed by Flaschenträger and Müller (*Hoppe-Seyl. Z.*, 1938, **251**, 52), and the improved method used in the isolation and determination of furan-2:5-dicarboxylic acid (I) from urine has fewer manipulations than that hitherto in use. The mean excretion value of I in urine of adults was 4.5 mg per day (compared with 2.5 mg by an earlier method), and it is claimed that the higher results may be due to a higher efficiency of extraction and to the fact that the extract of the urine was directly heated under reflux with 50%  $\text{H}_2\text{SO}_4$  at  $130^\circ$  to  $135^\circ$  for 1.5 to 2 hr., then steam-distilled with super-heated steam at  $140^\circ$  to  $160^\circ$ , and the residue extracted with ether from the same flask. Details of the procedure are given.  
B. B. BAUMINGER

**4407. New method for the determination of urea based on the urea-hypochlorite reaction.** J. Fuchs. *Chemiker Ztg*, 1960, **84** (4), 102-106.—The conditions for the quant. oxidation of urea with  $\text{HOCl}$  and the determination of the liberated  $\text{CO}_2$  as  $\text{BaCO}_3$  were studied. An apparatus and procedure are described which permit very dilute soln. of urea to be concentrated without loss of  $\text{CO}_2$ . For the pptn. of  $\text{BaCO}_3$ , 0.1 N  $\text{HCl}$  (6 ml) is added to the neutral urea soln. (50 ml) containing 20 to 100 mg of urea. Satd.  $\text{Ba}(\text{OCl})_2$  soln. (200 ml) is added and the flask is stoppered and set aside for 10 min. More  $\text{Ba}(\text{OCl})_2$  soln. is added until a flocculent ppt. separates and the soln. is slightly alkaline to phenolphthalein. The flask is then closed, well shaken and set aside for 2 min. The ppt. is filtered

off, washed with  $\text{H}_2\text{O}$  and ethanol, dried and weighed as  $\text{BaCO}_3$  or titrated. The max. error is  $< 0.6\%$ .  
G. BURGER

**4408. Colorimetric determination of urea [in whole blood, serum, plasma or urine].** C. J. Anderson and B. Strange (Finsen Inst., Copenhagen, Denmark). *Scand. J. Clin. Lab. Invest.*, 1959, **11** (2), 122-127.—The sample (diluted 1:20) (0.4 ml) is treated with 9 ml of 5% trichloroacetic acid soln., the protein ppt. is removed by filtration, and aliquots (1 ml) of the filtrate are placed in brown glass tubes together with 2 ml of 0.5% diacetyl monoxime soln. in 2.5% acetic acid, and 2 ml of 5.5% orthoarsenic acid soln. in 50%  $\text{H}_2\text{SO}_4$ . The resulting mixture is heated at  $90^\circ$  to  $100^\circ$  for exactly 15 min., then cooled in water at room temp. for 4 min., and the yellow product is determined photometrically at 478 m $\mu$ , against a water blank. Results are referred to a standard curve. This method can be used to determine urea concn. of 10 to 175 mg per 100 ml, and by using smaller aliquots, or by dilution, concn. of 350 mg per 100 ml or more may be determined. Recoveries of 95 to 105% are reported. The results are in good agreement with those obtained by the method of Van Slyke (*J. Biol. Chem.*, 1929, **83**, 449).  
D. B. PALMER

**4409. Fluorimetric determination of 4-pyridoxic acid in urine.** V. A. Bogdanova. *Vop. Pitan.*, 1959, **18** (5), 46-50; *Ref. Zhur., Khim., Biol. Khim.*, 1960, (4), Abstr. No. 4325.—Procedure.—Heat the urine in an acid medium to convert 4-pyridoxic acid (I) into its lactone. Adjust the pH to  $\approx 9$  with  $\text{Na}_2\text{B}_4\text{O}_7$  and measure the fluorescence which, under u.v. light, is blue-violet, whereas urine containing no I gives a blue-green fluorescence. Determine the degree of fluorescence, either with a fluorimeter or by direct visual comparison using a fluoroscope with a set of standard I soln.  
K. R. C.

**4410. Effect of coenzyme  $\text{Q}_{10}$  on the determination of tocopherol in animal tissue.** W. J. Pudlekiewicz and L. D. Matterson (Dept. of Poultry Sci., Univ. of Connecticut, Storrs, U.S.A.). *J. Biol. Chem.*, 1960, **235** (2), 496-498.—Coenzyme  $\text{Q}_{10}$  interferes with the determination of tocopherol by the Emmerie and Engel method (*Nature*, 1938, **142**, 873). If molecular distillation and chromatography on Florex XXS are included as steps in the analysis, the coenzyme  $\text{Q}_{10}$  is removed and the interference is eliminated.  
J. N. ASHLEY

**4411. Studies on the estimation of glycerol, fructose and lactic acid with particular reference to semen.** I. G. White (Dept. of Veterinary Physiol., Univ. Sydney). *Aust. J. Exp. Biol. Med. Sci.*, 1959, **37** (5), 441-450.—Semen is deproteinised with  $\text{ZnSO}_4$ - $\text{Ba}(\text{OH})_2$  or  $\text{ZnSO}_4$ - $\text{NaOH}$  mixtures. Fructose is determined in a portion of the filtrate photometrically at 480 m $\mu$  by the resorcinol method of Roe (*J. Biol. Chem.*, 1934, **107**, 15) as modified by Mann (*Brit. Abstr. C*, 1949, 141), the mixture being heated at  $80^\circ$  to  $85^\circ$  for 20 min. instead of the usual 10 min., to improve the colour stability. The remainder of the filtrate is then treated with  $\text{CuSO}_4$  and  $\text{Ca}(\text{OH})_2$  to remove fructose (Harvey and Higby, *Arch. Biochem. Biophys.*, 1951, **30**, 14) and centrifuged. In the supernatant liquid, glycerol is oxidised with  $\text{KIO}_4$ , and the formaldehyde so produced is determined photometrically at 580 m $\mu$  with chromotropic acid by the method of Lambert and Neish (*Brit.*

*Abstr. C*, 1951, 103) as modified by Ryley (*Biochem. J.*, 1955, **59**, 353). This procedure can also be used for the determination of glycerylphosphorylcholine. Lactic acid is determined in the supernatant liquid by a modification of the method of Barker and Summerson (*J. Biol. Chem.*, 1941, **138**, 535), by oxidation with  $\text{H}_2\text{SO}_4$  to acetaldehyde, which is determined photometrically at 565  $\text{m}\mu$  by means of 4-hydroxydiphenyl. The procedures are described, and it is shown that the concn. of lactic acid and fructose in the  $\text{ZnSO}_4$ - $\text{Ba}(\text{OH})_2$  filtrates are normally stable for at least 4 weeks at 4°. Contamination with micro-organisms can, however, cause a rapid fall in fructose concn., and the filtrates should preferably be stored in a deep-freeze, or treated with a wide-spectrum antibiotic.

D. B. PALMER

**4412. Benedict's solution as a developer in carbohydrate chromatography.** R. P. Murphy (Path. Dept., St. Finbarr's Hospital, Cork, Eire). *Nature*, 1960, **185**, 455-456.—Urine is de-ionised by being shaken first with Amberlite IR-120 ( $\text{H}^+$  form) for 20 min. and then with Amberlite IRA-400 ( $\text{OH}^-$  form) for 20 min. Aliquots (0.02 ml) of the treated urine and 0.01 ml each of 1% galactose and 1% glucose soln. are applied to the paper and developed by the descending technique for 24 hr. in a solvent system of either butanol-acetic acid- $\text{H}_2\text{O}$  or phenol satd. with  $\text{H}_2\text{O}$ ; this latter solvent is used in an atmosphere of ammonia. The chromatograms are dried at 80°, dipped into Benedict's reagent and dried for 30 min. at 105°. Reducing sugars appear as bright-orange spots on a pale-blue background. The spots are reasonably permanent, if stored in the dark.

S. BAAR

**4413. Separation of carbohydrate derivatives by gas-liquid partition chromatography.** C. T. Bishop and F. P. Cooper (Div. Appl. Biol., Nat. Res. Council, Ottawa, Canada). *Canad. J. Chem.*, 1960, **38** (3), 388-395.—All the possible tetra- and tri-O-methyl ethers of methyl  $\alpha$ - and  $\beta$ -D-glucopyranoside can be separated from a mixture (2 to 4  $\mu\text{g}$ ) by partition chromatography at 150° and 200°, with two columns (4 ft. by 5 mm), one containing butane-1:4-diol succinate polyester (polar) and the other containing Apiezon M (non-polar) as stationary liquid phases (20% of each) on Celite 545. The carrier gas is Ar and an ionisation detector is used; max. resolution is  $\approx 1000$  theoretical plates per ft., whilst the limit of detection is 0.01  $\mu\text{g}$ . With the exception of 3:4:6-tri-O-methyl-D-glucose, anomeric methyl glycosides of each isomer can be effectively separated. The six di-O-methyl-D-glucopyranosides are partly resolved as their methyl glycosides, whilst the four possible (and less volatile) mono-O-methyl-D-glucopyranosides can be completely resolved after conversion into the corresponding mono-O-methylpenta-O-acetyl-D-glucitols. The procedure permits the rapid and accurate determination of the relative amounts of the components in a mixture of methylated sugars. Thus, the molar ratio of methyl-2:3:4-tri-O-methyl- $\beta$ -D-xylopyranoside and methyl-2:3:4:6-tetra-O-methyl- $\alpha$ -D-glucopyranoside in a mixture can be determined with a mean deviation of  $\pm 0.5\%$  (5 analyses), in comparison with errors ranging from  $\pm 0.08$  to  $\pm 10\%$  for other methods.

W. J. BAKER

**4414. Determination of amylose in starch.** B. Carroll and H. C. Cheung (Dept. of Chem., Rutgers, The State Univ., Newark, N.J., U.S.A.). *J. Agric. Food Chem.*, 1960, **8** (1), 76-78.—The light absorption of Congo red at 500  $\text{m}\mu$  is increased by amylose

but not by amylopectin. With excess of amylose or even dextrin the absorption max. is independent of the chain length. This finding is applied to the determination of amylose in starch. *Procedure*—A buffer soln. ( $\text{NaOH}$ -K H phthalate at pH 4.2) (5 ml) and 0.1% starch soln. (5 ml) are placed in a 50-ml flask, and  $\approx 29$  ml of water and 10 ml of 0.0004 M Congo red are then added. The soln. is diluted to 50 ml and the extinction read at 500  $\text{m}\mu$ . An appropriate starch soln. is used as a blank. Corn amylose and corn amylopectin are used as standards. There is a considerable discrepancy between results obtained by the usual iodine method and the Congo red results, and this is considered to be due to changes of chain length affecting the iodine reading.

E. J. H. BIRCH

**4415. Micro-method for the colorimetric determination of N-acetyl groups in acid mucopolysaccharides.** J. Ludowieg and A. Dorfman (Chicago Univ., Ill., U.S.A.). *Biochim. Biophys. Acta*, 1960, **38** (2), 211-218.—In this method described, deacetylation of the dried sample (1 to 10  $\mu\text{moles}$  of acetyl) is carried out with 2 N methanolic HCl in a sealed tube at 100° for 4 hr. After cooling, the methyl acetate is distilled in the apparatus described, and the diluted distillate is treated with an alkaline hydroxylamine reagent. After 10 min., 0.75 M  $\text{HClO}_4$  is added, followed by a  $\text{FeCl}_3$ - $\text{HClO}_4$  reagent. The resulting ferric hydroxamate colour is measured after 5 to 10 min. at 520  $\text{m}\mu$ . Calibration is rectilinear. Factors affecting the deacetylation, colour development and reproducibility are discussed.

W. H. C. SHAW

**4416. Determination of hydroxyflavones in vegetable matter and industrial preparations.** G. A. Fedorova and V. A. Devyatnin. *Trudy Vses. Nauch. Vitamin. Inst.*, 1959, **6**, 251-256; *Ref. Zhur. Khim., Biol. Khim.*, 1960, (2), Abstr. No. 1444.—Dry the plant material at 105° for 3 to 6 hr. and grind it. Extract anthocyanins, pigments, fats, and resins from 1 to 3 g with boiling  $\text{CHCl}_3$ -isopropyl alcohol (1:1). Extract the air-dried residue with three 60-ml portions of methanol for 30 min. each. Dilute the extract to 200 ml with methanol. Filter, and dilute 10 ml of the filtrate to 25 ml with acetone. Filter off the ppt., transfer an aliquot (2 ml) of the filtrate to a photometric cell, add citrate-borate buffer (8 ml) and, after 10 min., determine the colour of the soln. at 470  $\text{m}\mu$ .

K. R. C.

**4417. Analytical assay of diosgenin.** S. Kaufmann, J. C. Medina and C. Zapata (Syntex, S. A., Mexico City). *Anal. Chem.*, 1960, **32** (2), 192-193.—The sample of crude diosgenin is sublimed at 180° under high vacuum. The diosgenin and the more volatile impurities are removed, leaving behind a dark residue. Re-sublimation at a temp. of 160° removes certain impurities from the original sublimate, leaving essentially pure diosgenin. The results compared well with those obtained by chromatography and countercurrent-extraction methods.

G. P. COOK

**4418. Analysis of biological amines by the techniques of chromatography, electrophoresis and paper chromatography.** J. Blass, A. Sarrafi and M. B. Nicolas (Inst. Pasteur, Service de Chim. Bactérienne, Garches, France). *J. Chromatography*, 1960, **3** (2), 168-177 (in French).—The techniques of chromatography, electrophoresis and a combination of the two have been used for the

separation of amines from broth cultures before and after hydrolysis. Electrophoresis separates most non-volatile amines from amino acids, but does not resolve them completely. Good separation is obtained by descending chromatography in butanol-acetic acid-water (25:6:25) in one direction, followed by electrophoresis in a second direction at right angles to the first. Volatile amines, after isolation by alkaline distillation, are separated by electrophoresis, except for butylamine and isobutylamine.  $R_F$  values, length of ionophoresis paths and limits of sensitivity for ninhydrin and various specific reagents are given.

P. D. PARR-RICHARD

**4419. Colorimetric determination of amino-acid concentration.** W. A. Vincent (Dept. Biol. Sci., Inst. Technol., Bradford, England). *Nature*, 1960, **185**, 530.—The sample (0.1 ml) is incubated overnight, in a conical centrifuge tube, with 3 ml of a 1% aq. suspension of  $\text{Cu}_3(\text{PO}_4)_2$  and 0.2 ml of BDH Universal buffer soln. (pH 7.0). If finely divided  $\text{Cu}_3(\text{PO}_4)_2$  is used, shaking is unnecessary. After centrifugation, 0.1 ml of the supernatant liquid, 3 ml of buffer soln. and 0.1 ml of 1% aq. Na diethylthiocarbamate soln. are mixed at room temperature, and the extinction is read at 440  $m\mu$  after 15 min. The colour is stable for at least 24 hr. Too high a concn. of Cu causes pptn. of the complex. For 50 to 1000  $\mu\text{g}$  of  $\alpha$ -alanine per ml the recovery was  $100 \pm 2\%$ . Peptides and proteins do not interfere.

S. BAAR

**4420. Photometric estimation of colour reactions on paper. Simple procedure for quantitative amino-acid determination.** K. H. Menke (Inst. für Tierzucht u. Tierfütterung, Univ., Bonn, Germany). *Z. anal. Chem.*, 1960, **172** (6), 423-428 (in German).—The method is valuable for the determination of amino acids separated by column chromatography. A 30 cm  $\times$  30 cm paper is divided into areas of 15 mm  $\times$  15 mm, treated with reagent (0.5 g of ninhydrin, 95 ml of *n*-butanol and 5 ml of 2 N acetic acid) and dried in air. The amino acids are then added in amounts of 0.01 to 0.015 ml and the paper dried again. After re-spraying with reagent, it is placed in a cabinet preheated to 100° and dried in a current of air. The transmittancy is measured at 630  $m\mu$  and at 530  $m\mu$ ; this eliminates error due to non-uniformity of the paper. A table of factors for conversion of colour readings to amounts of various amino acids in 0.2 M citric acid buffer at pH values of 3.25, 4.25 and 5.28 is given. The sensitivity for leucine is 0.2  $\mu\text{g}$  per ml; the standard deviation for 30  $\mu\text{g}$  per ml is  $\pm 0.83 \mu\text{g}$  (150 determinations).

P. D. PARR-RICHARD

**4421. Turbidimetric and titrimetric methods for the microbiological determination of amino acids: a unification of materials.** J. J. McGuire, S. S. Schiaffino and H. W. Loy (Div. of Nutrition, Food and Drug Admin., Dept. of Health, Education and Welfare, Washington, D.C., U.S.A.). *J. Ass. Off. Agric. Chem.*, 1960, **43** (1), 34-37.—The necessity of using a titrimetric method for the microbiological assay of amino acids, instead of the shorter turbidimetric method, when colour or extraneous turbidity interferes, makes it desirable to standardise for each amino acid a medium and an organism that is suitable for both methods. A formulation of a stock solution for the medium is given, and the organisms used for both methods are *Streptococcus faecalis* (ATCC 9790) for L-arginine; *Lactobacillus mesenteroides* (ATCC 8042) for L-cystine, L-histidine, L-lysine, L-methionine, L-phenylalanine,

L-threonine and L-tyrosine; and *Lb. plantarum* (ATCC 8014) for L-isoleucine, L-leucine, L-tryptophan and L-valine. Titrimetric and turbidimetric calibration curves are given.

E. J. H. BIRCH

**4422. Estimation of amino acids in biological material. VI. Methods for rapid estimation of amino acids and related ninhydrin-positive compounds.** G. Krampitz, R. Müller and M. Vollmers (Inst. Anat. Haustiere, Univ. Bonn). *Z. Tierphysiol. Tierernähr.*, 1959, **14**, 311-318.—Details are given of a rapid method of column chromatography with the resin Amberlite IR-120 (particle size 50 to 60  $\mu$ ) enclosed in Plexiglas. Neutral and acidic amino acids are separated on a column 150 cm in length, with buffer soln. 0.2 N with respect to  $\text{Na}^+$  and pH 3.25 and 4.25, at 50°; basic amino acids are separated on a 15-cm column, with 0.35 N buffer soln. at pH 4.26, and complex mixtures of basic amino acids and related ninhydrin-positive compounds are separated on a 50-cm column, with 0.38 N buffer soln. at pH 4.26 and 30°.

NUTR. ABSTR. REV.

**4423. Influence of certain factors on the intensity of the coloration of amino acids with unredacted ninhydrin on chromatographic paper.** M. Štefl, J. Tulach and A. Sovová (Dept. Chem., Sch. of Agric., Prague). *Coll. Czech. Chem. Commun.*, 1960, **25** (2), 435-441 (in German).—The intensity of the colour is influenced by the ninhydrin concn. and the solvent in which it is dissolved, the moisture in the paper and the temp. of the reaction, etc. It is stated that the max. colour intensity can be obtained by the use of acetone as the solvent, by maintaining a temp. of  $60^\circ \pm 0.5^\circ$  (a change of  $\pm 1^\circ$  seriously alters the intensity) and by carrying out the reaction for 25 to 30 min. The optimum water content can be achieved by saturating the drying chamber with water vapour and by adding 2 to 3% of water to the acetone; 0.01 ml of 1% ninhydrin soln. in acetone per sq. cm of paper is recommended.

J. ŽYKA

**4424. Automatic equipment for simultaneous determination of amino acids separated on several ion-exchange resin columns.** D. H. Simmonds and R. J. Rowlands (Waite Agric. Res. Inst., Univ. Adelaide, S. Australia). *Anal. Chem.*, 1960, **32** (2), 259-268.—The construction of automatic equipment to monitor simultaneously the percolates of eight ion-exchange columns is described. The unit fractionates the percolate from each column, treats each fraction with ninhydrin reagent and measures the resulting colour. The extinctions are numerically recorded on tape. Use of the equipment to analyse four insulin hydrolysates is described.

G. P. COOK

**4425. Direct amino-acid analysis by gas chromatography.** A. Zlatkis, J. F. Oró and A. P. Kimball (Univ. Houston, Tex., U.S.A.). *Anal. Chem.*, 1960, **32** (2), 162-164.—A special reactor-gas-chromatographic unit is employed. The amino-acid soln. is injected into a continuously flowing system whereby a heated micro-reactor containing ninhydrin oxidises the acids to aldehydes, which are then separated in a chromatographic column. After leaving the column the aldehydes are cracked to methane and water over a nickel catalyst. The water is removed by a drying column and the methane then determined by a thermal-conductivity cell. A mixture containing seven amino acids gave an error for the individual constituents of less than 5%, with one exception. As little as 1  $\mu\text{g}$  of amino acid can be detected.

G. P. COOK



**4426. Quantitative determination of proline by paper chromatography.** E. Hrabětová and J. Tupy (Inst. of Biology, Czech. Acad. Sci., Prague). *J. Chromatography*, 1960, **3** (2), 199-201 (in English).—After chromatographic separation of 5 to 20  $\mu$ g of proline, e.g., in the system *n*-butanol-acetic acid- $H_2O$  (4:1:5), the spots are detected by dipping the chromatogram in the reagent (1 g of isatin, 1.5 g of Zn acetate, 1 ml of acetic acid, 95 ml of isopropyl alcohol and 5 ml of  $H_2O$ ) and heating at 80° to 85° for 30 min. After washing the paper with warm  $H_2O$ , the spots are eluted in the dark for 15 min. with 5 ml of phenol saturated with  $H_2O$ , and the extinction of the eluate is measured at 610  $m\mu$ . Beer's law is followed for 0 to 20  $\mu$ g of proline.

P. D. PARR-RICHARD

**4427. Colorimetric method for determination of hydroxyproline in tissue hydrolysates.** K. I. Kivirikko and M. Lie Smaa (Dept. of Med. Chem., Univ. Helsinki, Finland). *Scand. J. Clin. Lab. Invest.*, 1959, **11** (2), 128-133.—The test soln. is shaken with  $\approx$  one-tenth of its weight of Permutit for 5 min. to remove ammonia. Aliquots of the supernatant liquid, standard soln. (1  $\mu$ g and 2  $\mu$ g), and water (blank) are thoroughly cooled in ice-water; 2 ml of ice-cold NaOBr soln. is then added, and after shaking and setting aside the mixture for 3 to 10 min., 0.1 ml of 16%  $Na_2SO_3$  soln. is added and the mixture is re-shaken. Finally 2 ml of 5% *p*-dimethylaminobenzaldehyde soln. in *n*-propanol is added and the mixture is acidified with 1 ml of 6 *N* HCl. After heating at 100° for 2.5 min., cooling in ice-water for 3 min., and setting aside at room temp. for 10 min., the coloured product is determined photometrically at 560  $m\mu$ . This method is suitable for soln. containing  $> 3 \mu$ g of hydroxyproline per ml. Tryptophan gives 0.12%, and tyrosine 0.03%, of the colour produced by hydroxyproline. Other amino acids do not interfere.

D. B. PALMER

**4428. Diazo reaction following chloramine-T oxidation as a sensitive and specific test for aspartic acid.** H. Stegemann and H. F. Griffin (Med. Forschungsanst. der Max-Planck-Ges., Silikose-Labor, Göttingen, Germany). *J. Chromatography*, 1960, **3** (2), 150-153 (in English).—When aspartic acid (I) is oxidised with chloramine T (II) the final product is an imidazole which reacts with diazotised sulphanilic acid (III) to give a stable orange-red colour. For the qual. detection of  $< 1 \mu$ g of I per sq. cm on chromatograms, spray well with a 0.02 *N* soln. of II in 50% methanol and dry thoroughly. Moisten the paper slightly with a fine spray of 10%  $Na_2CO_3$  soln., and 5 min. later with a 10% aq. suspension of diazotised III; the last two reagents should be applied 3 hr. after spraying with II. Some other amino acids give a similar reaction, but glutamic acid does not.

P. D. PARR-RICHARD

**4429. Rapid determination of methionine in crude proteins.** T. E. McCarthy and M. M. Paille (Dept. Chem., Boston Coll., Mass., U.S.A.). *Biochem. Biophys. Res. Commun.*, 1959, **1**, 29-33.—This is a modification of the method of Sullivan and McCarthy (*J. Biol. Chem.*, 1940, **133**, c-ci). Water (2 ml) and 10% NaOH soln. (6 ml) were added to protein (40 mg) in a test-tube which was then heated in an oil bath at 115° for 30 min. and inverted several times. After cooling, 10% sodium nitroprusside soln. (0.3 ml), 3% glycine soln. (2 ml) and heptafluorobutyric acid (4 ml) were added with intervals

of 10 min. between additions, and the extinction was measured at 510  $m\mu$ . Values for proteins agreed well with those in the literature. There was a considerable loss of methionine from unpurified gluten A after hydrolysis with 20% HCl even for 1 hr.

NUTR. ABSTR. REV.

**4430. New colorimetric method for the estimation of histidine and histamine.** P. M. Newman and J. H. Turnbull (Univ., Birmingham, England). *Biochem. J.*, 1960, **74** (2), 379-382.—The method is based on the formation of a violet colour when a soln. of the amino acid or amine is treated, at pH 11.0 to 12.0, with pyridine and aq.  $KI_3$  soln. The extinction is measured spectrophotometrically at 560  $m\mu$ , and the amount of material is ascertained from a standard graph. The violet colour appears to be formed only by compounds with the  $\beta$ -aminoethyl-4(or 5)-imidazole structure, with or without an  $\alpha$ -carboxylic acid substituent. Thus it is specific for histamine, and histidine and its methyl ester. Imidazole does not react and histidinamide gives only a very faint colour. Tryptophan and tyrosine give no colours under the conditions of the reaction, but they interfere with the colour formation, and when protein hydrolysates and biological materials are examined these amino acids and other interfering substances are removed by selective adsorption of histidine and histamine by an ion-exchange resin. The intensity of the violet colour is decreased in the presence of  $Cu^{2+}$ ,  $Zn^{2+}$  and  $Fe^{2+}$ , probably by complex formation with the histidine;  $Cu^{2+}$  also react with the pyridine to give a blue complex. The intensity of the violet colour is also decreased by strong nucleophilic anions such as  $SCN^-$ . The method, which can be used for the determination of 2 to 60  $\mu$ g of histidine or histamine per ml, does not seem to be applicable to the determination of combined histidine in an intact protein. The accuracy of the results is within  $\pm 5\%$ .

J. N. ASHLEY

**4431. Effect of oxygen upon the micro-determination of histidine with the aid of the Pauly reaction.** L. A. A. Sluyterman (N. V. Philips' Gloeilampenfabrieken, Eindhoven, The Netherlands). *Biochim. Biophys. Acta*, 1960, **33** (2), 218-221.—Instability of the colour formed on treating histidine with diazosulphanilic acid and making alkaline is attributed to the presence of O in the reaction mixture. The effect can be minimised by the addition of ethanol. A paper-chromatography system for separating histidine from protein hydrolysates and its subsequent colorimetric determination by the improved method are described.

W. H. C. SHAW

**4432. [Determination of] canavanine in the Leguminosae.** E. A. Bell (Dept. of Biochem., King's Coll., London, England). *Biochem. J.*, 1960, **75** (3), 618-620.—The sensitivity of the Fearon and Bell method (*Anal. Abstr.*, 1955, **2**, 1362) for the colorimetric determination of canavanine (2-amino-4-guanidinoxybutyric acid) is increased approx. 30-fold by determination of the extinction spectrophotometrically at 522  $m\mu$ .

J. N. ASHLEY

**4433. Ultra-violet spectrophotometry of serum proteins.** R. D. Strickland, P. A. Mack, T. R. Podleski and W. A. Childs (Res. Div., Veterans Admin. Hospital, Albuquerque, N.M., U.S.A.). *Anal. Chem.*, 1960, **32** (2), 199-202.—Ultra-violet spectrophotometry has been used to estimate serum-proteins fractions separated from blood

electrophoretically. The results of determinations of the tyrosine and tryptophan composition of these proteins showed wide variations, and indicated that the method was unsatisfactory for quant. assays.

K. A. PROCTOR

**4434. Iodine-131 as an "amplifier" in paper electrophoresis of protein solutions of low concentrations.** O. P. Foss (Ullevål Hospital, Oslo, Norway). *Scand. J. Clin. Lab. Invest.*, 1959, **11** (2), 169-171.—The paper-electrophoretic separation of proteins from soln. containing < 3 g per 100 ml is adversely affected by absorption of protein by the paper. This can be overcome if the paper is pre-treated with a barbitone buffer soln. (0.1 M, pH 8.6) containing 10% of human serum. The dilute protein soln. under investigation is iodinated with  $^{131}\text{I}$  before separation according to the method of Foss (*Ibid.*, 1958, **10**, 418). Results agree with those obtained by standard methods.

D. B. PALMER

**4435. Separation and determination of free purines, pyrimidines and nucleoside in cod muscle.** N. R. Jones (D.S.I.R., Torry Res. Sta., Aberdeen, Gt. Britain). *Analyst*, 1960, **85**, 111-115.—The homogenate of the dissected muscle with chilled  $\text{HClO}_4$  is filtered rapidly at 0° and the pH of the filtrate is immediately adjusted to 6.5 with N KOH. After 30 min. at 0°, crystallised  $\text{KClO}_4$  is removed. An aliquot (= 5 g of tissue) is run through a column of Dowex I (formate) to remove nucleotides. The pH of the combined percolate and washings is adjusted to 11 to 12 with aq.  $\text{NH}_3$ , the liquid is run through a Dowex I (chloride) column, and the column is eluted in a special apparatus with a gradient soln. increasing in  $\text{Cl}^-$  and  $\text{Na}_2\text{B}_4\text{O}_7$  content and diminishing in pH, fractions being collected. The extinction of each fraction is measured at 260  $\mu\text{m}$ , and those fractions corresponding to individual peaks are combined; HCl is added to give a concn. of 2 N, and extinctions are measured at the appropriate maxima for evaluation against the known molar extinction coeff. Recovery of individual added bases ranged from 98 to 100%.

A. O. JONES

**4436. Components of nucleic acid and their analogues. VI. Polarographic determination of 6-azauracil and 6-azauridine.** J. Krupička and J. Gut (Dept. of Org. Synth., Chem. Inst., Acad. Sci., Prague). *Coll. Czech. Chem. Commun.*, 1960, **25** (2), 592-595 (in German).—Uracil is polarographically inactive, whereas 6-azauracil (I) and 6-azauridine (6-azauracilriboside) (II) can be differentiated and determined polarographically. In phosphate buffer soln. (pH 6.9) a single wave appears, which corresponds to the total amount of I and II, whereas in borate buffer soln. the height of the wave of II is only one-half that of I. By measurement of the waves in both buffer soln. the content of I and II can be calculated by means of a simple mathematical relation and reference to calibration curves. The determination can also be carried out in acid medium (pH 2) and can thus be used for the determination of II in blood serum and urine. Good results were also obtained in 20 N  $\text{H}_2\text{SO}_4$ .

J. ZYKA

**4437. Evaluation of the Theorell method for the determination of total serum [or plasma] cholesterol.** K. Cramér and B. Isaksson (Central Clin. Lab., Sahlgrenska Sjukhuset, Gothenburg, Sweden). *Scand. J. Clin. Lab. Invest.*, 1959, **11** (2), 213-216.—Serum or plasma (1 ml) is added dropwise to 20 ml

of acetone-ethanol (1:1) with constant shaking, and the mixture is brought to boiling-point. When cold, the soln. is filtered through a fat-free paper into a 25-ml flask, and the filtrate is made up to vol. with the solvent. Aliquots (2 ml) of the filtrate are evaporated to dryness at 100° on a boiling-water bath, and the residues are dissolved in 1 ml of  $\text{CHCl}_3$ ; 2 ml of acetic anhydride and 0.25 ml of acetic acid -  $\text{H}_2\text{SO}_4$  (9:1) are added, and the reaction mixture is heated at 35° for exactly 13 min. The coloured reaction product is measured photometrically at 660  $\mu\text{m}$  within 10 min., with recrystallised cholesterol as the standard. Beer's law is obeyed for cholesterol concn. up to 1 g per 100 ml. Practical details are discussed, and the results obtained are compared with those by the more elaborate method of Sperry and Webb (*J. Biol. Chem.*, 1950, **187**, 97). It is shown that the present method, which is a modification of that due to Theorell (*Biochem. Z.*, 1926, **175**, 296; 1930, **223**, 1; *Z. ges. exp. Med.*, 1931, **75**, 699), has a lower standard deviation, but gives values 4-6% greater than the method of Sperry and Webb. This may be due to the extraction of other coloured compounds, or to losses of cholesterol during the many manipulations of the Sperry and Webb technique. The Theorell method is simple, reliable, and sufficiently accurate for routine serial analyses.

D. B. PALMER

**4438. Paper-chromatographic fractionation of plant steryl esters.** A. Kuksis and J. M. R. Beveridge (Queen's Univ., Kingston, Ontario). *Canad. J. Biochem. Physiol.*, 1960, **38** (2), 95-106.—The  $\text{C}_{22}$  to  $\text{C}_{28}$  saturated, and  $\text{C}_{18}$  unsaturated fatty acid esters of  $\beta$ - and  $\gamma$ -sitosterol, stigmasterol, ergosterol, stigmasterol and  $\gamma$ -sitosterol were satisfactorily separated by ascending reversed-phase paper chromatography, with liquid paraffin as the stationary phase, and (i) methanol -  $\text{CHCl}_3$  - water - acetic acid (10:10:1:1), (ii) propionic acid - water (9:1), (iii) acetic acid -  $\text{CHCl}_3$  - water (15:4:1), or (iv) butyric acid - water (3:1) as the mobile phase. The paper was impregnated with liquid paraffin by immersion in a 5% soln. in  $\text{CHCl}_3$ , blotting, and drying. Solvents (i) or (iv) were most suitable for the separation of esters of the long-chain fatty acids, and (iii) for those of shorter chain-length;  $R_F$  values were proportional to the degree of unsaturation of the esters examined, and inversely proportional to their mol. wt. The introduction of a double bond into the sterol nucleus caused an increase in  $R_F$  of approx. one-half of that observed when the introduction was into either the fatty acid or sterol side-chain. This has been correlated with the total number of ethylenic H atoms present.

D. G. MOSS

**4439. Combined estimation of cortisol and 11-deoxycortisol in plasma as Porter-Silber chromogens.** E. M. Gold, B. Serena and S. Cook (Metab. Unit for Res. in Arthritis and Allied Dis., Univ. of Calif. Sch. of Med., San Francisco, U.S.A.). *J. Clin. Endocrin. & Metabolism*, 1960, **20** (2), 315-326.—The method of Peterson *et al.* (*Anal. Chem.*, 1957, **29**, 144) is modified by evaporating the extracting solvent before addition of the colour reagent. In the original method nearly 50% of the 11-deoxycortisol is lost in this step. The dichloromethane (I) extracts are evaporated to dryness at 37° to 40° in a current of air filtered through glass wool. The sides of the centrifuge tubes are washed down with 2 to 3 ml of I and the extracts are again evaporated to dryness. The dry residues are dissolved in 0.5 ml of I, the colour and blank

reagents are added, and the tubes are shaken mechanically for 10 min., centrifuged at 2500 r.p.m. for 5 min. and the 0.5-ml layers of **I** are discarded by careful aspiration. Other details of procedure are as originally described by Peterson *et al.*

H. F. W. KIRKPATRICK

**4440. Quantitative determination of cyanoacetic acid as an enzymic product of  $\beta$ -aminopropionitrile.** H. W. Sievert, S. H. Lipton and F. M. Strong (Wisconsin Univ., Madison, U.S.A.). *Arch. Biochim. Biophys.*, 1960, **86** (2), 311-315.—Tissue samples are homogenised and acidified, and the cyanoacetic acid (**I**) is extracted with ethyl acetate, which, after the addition of aq.  $\text{Na}_2\text{CO}_3$ , is evaporated to dryness. The residue is dissolved in water and an aliquot containing 1 to 7  $\mu\text{g}$  of **I** is treated with ice-cold diazotised sulphanilic acid. After 10 min. at room temp., excess of aq.  $\text{Na}_2\text{CO}_3$  soln. is added, and the extinction at 490  $m\mu$  is plotted at 1-min. intervals until max. extinction is reached after 3 to 5 min., when fading begins. Calibration is rectilinear. The rate of formation of **I** from  $\beta$ -aminopropionitrile in the presence of liver homogenates from various species is studied.

W. H. C. SHAW

**4441. Fluorimetric method for measuring the activity in serum of the enzyme lactic dehydrogenase.** T. Laursen (Rigshospitalet, Copenhagen, Denmark). *Scand. J. Clin. Lab. Invest.*, 1959, **11** (2), 134-137.—This method is an application of previously published methods for the determination of glutamic-pyruvic and glutamic-oxalacetic transaminases (*Anal. Abstr.*, 1959, **8**, 1493; 1960, **7**, 696). Diluted serum is incubated with a substrate consisting of nicotinamide, pyruvate and reduced diphosphopyridine nucleic acid, the diphosphopyridine nucleic acid produced by the reaction being determined fluorimetrically as the ethyl methyl ketone condensation compound. The method is sensitive, reproducible, and suitable for routine work. Normal values are reported as  $13 \pm 4$  units.

D. B. PALMER

**4442. Colorimetric method for the estimation of succinic dehydrogenase activity.** M. M. Nachlas, S. I. Margulies and A. M. Seligman (Dept. of Surg., Sinai Hosp. of Baltimore, Inc., Md., U.S.A.). *J. Biol. Chem.*, 1960, **235** (2), 499-503.—The simple and sensitive assay depends on the use of phenazine methosulphate as the intermediate electron carrier between the reduced enzyme and the reagent (2-*p*-iodophenyl-3-*p*-nitrophenyl-5-phenyltetrazolium chloride). The presence of gelatin in the reaction mixture helps to keep the small amount of formazan formed in fine colloidal suspension, so that Beer's law is applicable in the range of measurement (40 to 240  $\mu\text{g}$  of formazan). A photo-electric colorimeter is used with a 540- $m\mu$  filter, and the amount of formazan, and hence of dehydrogenase, is ascertained from a standard graph obtained by means of reduced diphosphopyridine nucleotide. It is not necessary to extract the formazan into an organic solvent.

J. N. ASHLEY

**4443. Studies on sulphasates. XXVIII. Preparation of substrates for the assay of glycosulphatase.** A. G. Lloyd (Dept. of Biochem., Univ. of Wales, Newport Rd., Cardiff). *Biochem. J.*, 1960, **75** (3), 478-482.—Methods are described for the preparation of the crude potassium salts of glucose 6-O-sulphate, galactose 6-O-sulphate, N-acetylglucosamine 6-O-sulphate and N-acetylgalactosamine monosulphate. The pure potassium salts are

obtained by zone electrophoresis on cellulose columns.

J. N. ASHLEY

**4444. Viscosimetric micro-determination of hyaluronidase activity in biological fluids.** Yu. V. Natochin. *Byul. Eksperim. Biol. i Med.*, 1959, **47** (8), 118-121; *Ref. Zhur., Khim., Biol. Khim.*, 1960, (6), Abstr. No. 7321.—Determine the viscosity in small (0.5 ml) amounts of biological fluids with a capillary-type viscometer from the time of flow of a mixture consisting of the test soln., a buffer, and hyaluronate (**I**) before and after a 20-min. incubation. To obtain the enzyme activity of the test soln., express the reduction in the viscosity of the substrate as a percentage of the original figure. Fully depolymerised **I** serves as a control.

K. R. C.

**4445. Spectrophotometric assay of bovine pancreatic ribonuclease by the use of cytidine 2':3'-phosphate.** E. M. Crook, A. P. Mathias and B. R. Rabin (Univ. Coll., London, England). *Biochem. J.*, 1960, **74** (2), 234-238.—The assay is based on the change in the u.v. absorption spectrum which results from the hydrolysis of cytidine 2':3'-diphosphate by the ribonuclease. The extinction is measured at 284  $m\mu$  (or within the range 284 to 290  $m\mu$ ), and the amount of enzyme is ascertained from a standard graph. Suitable conditions for the assay include a pH value of  $\approx 7.0$ , a fairly high ionic strength to minimise the effects of changes in the substrate during the hydrolysis, an initial substrate concn. of 0.1 to 0.3 mg per ml, and a slit width as narrow as possible, which must be kept constant during a set of measurements, and a temp. of  $25^\circ \pm 0.2^\circ$ . Two methods are given for the determination of the extinction at zero time. Simple modifications are described which allow rapid assays, of somewhat lower precision, to be made.

J. N. ASHLEY

See also Abstracts—4090, Isotopes of Sr in urine. 4187, Silicon in urine. 4266, Determination of Fe. 4301, Determination of C in  $^{14}\text{C}$ -labelled comp. 4331, Determination of sugars. 4353, Phenol in soln. containing tyrosine, chymotrypsin, etc. 4455, Assay of cortisone and cortisol. 4457, Aucubin in *Plantago* spp. 4491, Chromatography of sterols. 4506, Tocopherols in animal tissues. 4526, Measurement of  $\alpha$ -radio-activity in biol. materials. 4547, Van Slyke gas-analysis apparatus. 4551, Simplified Haldane's apparatus. 4569, Apparatus for electrophoresis on cellulose powder. 4570, Buffers for electrophoresis.

#### Pharmaceutical analysis

**4446. New colour test for heroin (diamorphine).** M. Lerner (U.S. Customs Lab., Baltimore, Md., U.S.A.). *Anal. Chem.*, 1960, **32** (2), 198.—The reagent is prepared by mixing 12 ml of conc.  $\text{HNO}_3$  with 38 ml of 85%  $\text{H}_3\text{PO}_4$ . To 10 drops of this soln. in a centrifuge tube is added 3-25 ml of  $\text{CHCl}_3$  containing 0.5% of ethanol, and the sample of diamorphine is washed in with  $\text{CHCl}_3$ . The tube is stoppered and shaken vigorously for 10 sec. A colour develops in the aq. phase, the shade being dependent on the concn. of diamorphine; 10  $\mu\text{g}$  can readily be detected. The method is not affected by the presence of the usual diluents or adulterants.

G. P. COOK

**4447. Application of the modified Vitali-Morin reaction to the assay of some preparations from the [Fr.] Codex with solanaceous base.** P. Febvre and

G. Roret (Fac. de Méd. et Pharm., Clermont-Ferrand, France). *Ann. Pharm. Franç.*, 1960, **18** (1-2), 45-48.—The modified Vitali-Morin method (Febvre, *Anal. Abstr.*, 1958, **5**, 3108) is applied to further pharmaceutical preparations. Procedures for preparing various drugs before the determination are given. Belladonna, stramonium or hyoscyamus powders (1 g) are moistened with 1 ml of dil. aq.  $\text{NH}_3$  and shaken for 0.5 hr. with 20 ml of diethyl ether- $\text{CHCl}_3$  (3:1, w/w). The extraction is repeated, the combined filtrates are distilled, and the residue is re-dissolved in ether- $\text{CHCl}_3$ . The alkaloids are extracted with 0.1 N  $\text{H}_2\text{SO}_4$  and evaporated to dryness in preparation for the determination. For tinctures, 1 g is shaken with 5 ml of ether- $\text{CHCl}_3$  and 2 drops of aq.  $\text{NH}_3$ , and the aq. layer is gelled by 0.1 g of powdered gum tragacanth. The coagulum is then extracted and the extract treated as for the powder. The method is compared with official methods. E. J. H. BIRCH

4448. Quantitative spectrophotometric determination of apatropine in presence of atropine. L. Mathies and H. G. Leemann (Pharmaz. Dept., Sandoz A.-G., Basle, Switzerland). *Z. anal. Chem.*, 1960, **172** (6), 430-432 (in German).—Rapid determination of the highly toxic impurity apatropine by u.v. spectrophotometry is described. The extinction at 244 m $\mu$  is directly proportional to the percentage of apatropine present; the accuracy of measurement for amounts of 1 to 10% is  $\pm 0.5\%$ . The purity of the alkaloids used for calibration was checked by paper chromatography. P. D. PARR-RICHARD

4449. Oscillopolarographic determination of quinine alkaloids. II. L. Molnár and K. Molnárová (Dept. Natural Compounds, Chem. Inst., Acad. Sci., Bratislava, Czechoslovakia). *Chem. Zvesti*, 1960, **14** (1), 21-31.—The relation between the shape of the oscillogram and the constitution of quinine and its derivatives was studied. The idealised oscillogram, characterised by three cut-ins, is described. The influence of the substituent on the depth of the cut-ins was investigated. The shape of the oscillogram is influenced by the length of the chain of the substituent on the carbon atom in the 6 position. The oscillographic curves registered with one cycle on one drop are described and compared with those obtained on the dropping electrode in LiCl soln. as the electrolyte. Calibration curves of the dependence of the depth of the cut-in on the concn. of the quinine derivative were constructed. The positions of the cut-ins of 12 quinine derivatives were measured. J. ŽYKA

4450. Studies on the fluorimetric analysis of drugs. VI. Analysis of cotarnine chloride. Yoji Ichimura (National Hyg. Lab., Tamagawa-yoga, Setagaya-ku, Tokyo). *Japan Analyst*, 1959, **8** (9), 557-561.—The max. fluorescence of cotarnine (I) is at 500 to 505 m $\mu$  in water, 480 m $\mu$  in dil. NaOH soln., 530 m $\mu$  in ethanol and 470 m $\mu$  in ethanolic KOH soln. The intensity in water increases at pH > 11.5, pH 12-8 being suitable for analysis. The working curve is linear for 0.1 to 1  $\mu\text{g}$  of I per ml. The ethanolic soln. of I is also useful for analysis (480 m $\mu$ ). I on filter-paper gives max. fluorescence at 480 m $\mu$ , irrespective of the developing agent. K. SAITO

4451. Photometric micro-determination of lobeline. F. Kaczmarek (Państwowy Inst. Nauk. Lekniczych Surowców Roślinnych, Poznań).

*Biul. Inst. Roślin Lekniczych*, 1960, **6** (1), 1-17.—The method described involves a chromatographic separation of lobeline on S. & S. 2045 b.M. chromatographic paper which is impregnated with a soln. containing 9 ml of formamide, 0.8 g of ammonium formate, 1 ml of formic acid and 20 ml of abs. methanol. The paper is dried at room temperature for 30 min. and spots of a soln. of lobeline or lobelia alkaloids in  $\text{CHCl}_3$ -methanol (9:1) containing 10 to 50  $\mu\text{g}$  of lobeline are placed on the starting line, with a spot of pure lobeline soln. alongside for identification purposes. The paper is developed with  $\text{CHCl}_3$ -benzene (9:1) saturated with formamide at  $20^\circ \pm 2^\circ$  for 5 to 6 hr. The chromatogram is dried at  $90^\circ \pm 10^\circ$  and sprayed with Amelink (modified Dragendorff) reagent. The spot due to lobeline is cut out and shaken for 3 min. in a stoppered tube with 2 ml of buffered Tropaeolin OO soln. (pH 3.4) and 5 ml of  $\text{CHCl}_3$ , then centrifuged for 2 min. An aliquot of the  $\text{CHCl}_3$  phase is transferred to a 2-cm cell and the extinction is read in a Pulfrich photometer with a S42 filter. A blank is treated similarly, and the lobeline content is then read from a calibration curve. The mean error is  $\pm 2.0\%$ . M. MORAN

4452. Colorimetric determination of esters of veratrum alkaloids. L. Molnár and E. Domková (Dept. Natural Products, Chem. Inst. Acad. Sci., Bratislava, Czechoslovakia). *Českosl. Farm.*, 1960, **9** (2), 63-66.—The method is based on alkaline hydrolysis of the esters in the presence of hydroxylamine, and the colorimetric determination of the hydroxamic acid thus produced with  $\text{Fe}^{3+}$ . Procedure—To a soln. of the sample in anhyd. ethanol (1 to 2 ml, containing  $\approx 2$  mg of esters) add 3 ml of a freshly prepared soln. of hydroxylamine (heat 25 ml of a 12.5% soln. of hydroxyammonium chloride in anhyd. methanol under reflux for 5 to 10 min., add 25 ml of a 12.5% soln. of NaOH in the same solvent and filter off the pptd. NaCl). Heat for 30 min. at  $50^\circ$  on a water bath. Cool and dilute to 25 ml with a soln. of  $\text{Fe}(\text{ClO}_4)_3$ . (To 0.8 g of powdered iron add 3 ml of  $\text{H}_2\text{O}$  and, slowly, 10 ml of 70%  $\text{HClO}_4$ ; dilute with 7 ml of  $\text{H}_2\text{O}$  and evaporate nearly to dryness. Dilute the residue to 100 ml with anhyd. ethanol.) After 40 min. measure the extinction at 530 m $\mu$ . Carry out a blank. Compare with a calibration curve (4 to 30 mg per 100 ml). The max. error is  $\pm 2\%$ . J. ŽYKA

4453. Iodine as a colorimetric reagent. I. Assay methods for caffeine, colchicine and reserpine. J. E. Gardner and S. J. Dean (School of Pharm., Univ. of Calif. Medical Center, San Francisco). *Drug Standards*, 1960, **28** (2), 50-52.—Place  $\text{H}_2\text{O}$  (3 ml) in a sintered-glass funnel of capacity 60 ml and apply sufficient positive pressure from below to prevent flow of liquid. Add 3 N iodine (1 ml) and a 1% soln. of caffeine or reserpine (5 ml) and mix. Add 50%  $\text{H}_2\text{SO}_4$  (0.5 ml), set aside for 10 min. with gentle mixing, and then apply suction from below. Wash the ppt. with 0.01 N iodine containing 10% of  $\text{H}_2\text{SO}_4$  (25 ml), dissolve the residue in acetone, dilute to 25 ml and measure the extinction at 525 m $\mu$ . The procedure is similar for colchicine, but 3 ml of 3 N iodine is used and the suspension is set aside for 30 min. before filtration. The estimated coeff. of variation are caffeine  $\pm 2.3\%$ , colchicine  $\pm 5.4\%$ , and reserpine  $\pm 6.9\%$ . A. R. ROGERS

4454. Determination of chlortetracycline and bromtetracycline in tetracycline produced by fermentation. A. Sauciu (Inst. Pharm.-Chem. Res., Iași).



*Rev. Chim., Bucharest, 1960, 11 (2), 113-114.*—A colorimetric micro-method based on the replacement of  $\text{SCN}^-$  by  $\text{Cl}^-$  in  $\text{Hg}(\text{SCN})_2$  is used for the simultaneous determination of Cl and Br. Standard curves are prepared as follows. A measured vol. of a standard is diluted to 15 to 18 ml with water. The mixture is treated with exactly 25 ml of a 0.6% methanolic soln. of  $\text{Hg}(\text{SCN})_2$  and 2.5 ml of a 12% soln. of  $(\text{NH}_4)_2\text{SO}_4 \cdot \text{Fe}_2(\text{SO}_4)_3$  in  $\text{HNO}_3$  and cooled to  $20^\circ \pm 0.5^\circ$ . It is then diluted to 25 ml with water and after 10 min. the extinction is measured by means of a Pulfrich photometer with a 547 filter against blanks prepared in the same way. *Procedure*—The weighed sample (1 to 25 mg) is treated with 3 ml of an oxidising soln. (100 ml of conc.  $\text{H}_2\text{SO}_4$  containing 10 g of  $\text{K}_2\text{Cr}_2\text{O}_7$  and 2 g of  $\text{AgNO}_3$ ; the whole is heated to  $140^\circ$  for 15 min.) in a bath maintained at  $120^\circ$  to  $140^\circ$ . After 15 min. a weak current of air via a soln. of 25% KOH as scrubber is passed for 15 min. through the vessel into an absorption tube containing 2%  $\text{H}_2\text{O}_2$  soln. (10 ml); the absorbed soln. is washed out of the tube into a 25-ml flask (soln. A). To remove Br, 10 ml of soln. A is treated with 0.3 ml of N NaOH and  $\approx 0.1$  g of  $\text{MnO}_2$ . After 10 to 15 min., when all  $\text{H}_2\text{O}_2$  is decomposed, 1 ml of N  $\text{H}_2\text{SO}_4$  and  $\approx 0.1$  g of  $\text{PbO}_2$  are added, and the mixture is heated for 10 min. on the water bath. It is then cooled, filtered into a 25-ml flask and treated as for construction of the standard curve, and the extinction  $E_1$  corresponding to the  $\text{Cl}^-$  present is determined. To determine the extinction corresponding to  $\text{Cl}^- + \text{Br}^- = E_2$ , 10 ml of soln. A is taken and the curve prepared as above. The Br content is then calculated from the value  $E_2 - E_1$ , using the standard curve for Br. Finally the content of chlor- and brom-tetracycline is calculated by taking into account the N content. H. SHER

4455. Colorimetric assay of cortisone and cortisol. Sultana Ansari and Riaz Ahmed Khan [Glaxo Laboratories (Pakistan) Ltd., Karachi]. *J. Pharm. Pharmacol.*, 1960, 12 (2), 122-125.—The method of Schulz and Neuss (*cf. Anal. Abstr.*, 1958, 5, 1323) has been modified. The results are higher than those obtained by the tetrazolium method of the U.S.P. XV. Penicillin, streptomycin and neomycin do not interfere. *Procedure*—Extract ointments, lotions or injections with 90% ethanol, filter and dilute suitably. Extract tablets with  $\text{CHCl}_3$ , filter, evaporate and dissolve the residue in 90% ethanol. To 5 ml of the soln., containing  $< 125 \mu\text{g}$  of cortisone (I) or  $< 200 \mu\text{g}$  of cortisol (II), add a 0.5% soln. of 2:6-di-*tert*-butyl-*p*-cresol in 90% ethanol (5 ml) and N NaOH (10 ml) and heat under reflux at  $100^\circ$  for 30 min. Cool rapidly, filter, and measure the extinction at  $471 \text{ m}\mu$  (for I) or  $625 \text{ m}\mu$  (for II) 20 min. after starting to cool. Subtract a reagent blank. A. R. ROGERS

4456. Photometric determination of the anthraquinone components of alder buckthorn. R. Paris and M. Durand (Lab de Mat. Méd., Fac. de Pharm., Paris, France). *Ann. Pharm. Franç.*, 1959, 17 (10-12), 593-599.—Alder buckthorn bark is extracted with methanol (for 0.5 to 3 hr., or rapidly by boiling) and 1 to 5  $\mu\text{l}$  of the extract is chromatographed on paper by the ascending technique, with Partridge's solvent, Viéjo's azeotropic solvent (*cf. Paris and Viéjo, Ibid.*, 1955, 13, 424) or butanol-formic acid-water (4:1:5). The  $R_F$  values of frangula emodin, frangulin and glucofrangulin (which have been obtained in larger quant. from the bark for control and calibration) and of other

unidentified spots are recorded and depend more on the nature of the paper than that of the solvent. The colour of the spots in u.v. and ordinary light, with or without spraying with 5% KOH soln., 5% methanolic Mg acetate soln. (and heating to  $100^\circ$ ) or 10% aq.  $\text{Na}_2\text{B}_4\text{O}_7$  soln., are reported. The spots are quant. assessed with a photodensitometer on the paper, and the method is applied to a commercial alder buckthorn bark. E. J. H. BIRCH

4457. The aucubin content in some domestic *Plantago* species and in some galenicals [determination and identification]. G. Dušínský and M. Tylová (State Inst. for Control of Drugs, Bratislava, Czechoslovakia). *Českosl. Farm.*, 1960, 9 (2), 60-62.—*Procedure*—Extract the dried and powdered sample (0.5 to 1 g) with diethyl ether (3 hr. with 10 ml and twice for 2 hr. with 5 ml). Remove the ether from the combined extracts by evaporation in air and then extract with a ten-fold excess of 50% ethanol for 24 hr. Filter and press the residual sample, wash with a small vol. of ethanol and repeat the procedure till no more aucubin can be detected in the filtrate. Dilute the combined filtrates with 50% ethanol to a known vol. and to an aliquot (1 ml = 10 to 80  $\mu\text{g}$  of aucubin) add 96% ethanol (3 ml) *p*-dimethylaminobenzaldehyde soln. (2% in 20% HCl) (1 ml), 20% HCl (1 ml) and  $\text{H}_2\text{O}$  (4 ml). Mix, and heat for exactly 8 min. on a water bath at  $65^\circ$ . Cool and maintain at  $20^\circ$  for 15 min., then measure the extinction of the blue soln. spectrophotometrically at  $595 \text{ m}\mu$  and compare with a calibration curve. *Identification of aucubin by paper chromatography*—Place the extract (0.025 to 0.05 ml) on Whatman No. 1 paper and chromatograph with butanol-acetic acid- $\text{H}_2\text{O}$  (4:1:5). Spray with *p*-dimethylaminobenzaldehyde soln. and dry in a stream of warm air; blue spots ( $R_F = 0.36$ ) indicate aucubin. J. ZVKA

4458. Complexometric titration in analysis of organic pharmaceuticals. III. The assay of mepacrine and its preparations. Yuan-Yau Chou, Jing-Ling Chen and Ju-Cheng Hsu (Wu-Han Municipal Drug Bureau, China). *Acta Pharm. Sinica*, 1960, 8 (2), 61-65.—The method described is based on the quant. pptn. of mepacrine by  $\text{K}_2\text{Cr}_2\text{O}_7$  (I) in accordance with a 1:1 molecular ratio and on the back-titration of the excess of I with EDTA. The sensitivity of the test is 1 in  $5 \times 10^4$  and the reaction is not appreciably affected by changes in temp. and acidity. The method is suitable for the determination of mepacrine in the form of hydrochloride or methanesulphonate. *Procedure*—Weigh the sample containing 0.8 milliequiv. of mepacrine into a 50-ml flask and dissolve in water (30 ml). Add 0.1 M I (10 ml), shake, and dilute to volume. After 30 min. filter, reject the first 10 ml and to the subsequent 25 ml add aq.  $\text{NH}_3 \cdot \text{NH}_4\text{Cl}$  buffer soln. (5 ml) and Eriochrome black T indicator (0.5 ml) and titrate the excess of I with 0.02 M EDTA (disodium salt) to a pure blue end-point. The results obtained are in good agreement with those obtained by an established gravimetric method. The method may be applied to mepacrine tablets, but 15% NaCN soln. (5 ml) should be added to obviate the interference by magnesium stearate in the titration with EDTA. S. H. YUEN

4459. Quantitative separation of N-acetyl-*p*-aminophenol and *p*-aminophenol by ion-exchange chromatography. K. T. Koshy and J. L. Lach (State Univ. of Iowa, Coll. of Pharm., Iowa City,

U.S.A.). *Drug Standards*, 1960, **28** (2), 53-56.—Apply an aq. soln. (5 ml) containing *p*-acetamidophenol (**I**) (< 5 mg) and *p*-aminophenol (**II**) (< 1 mg) to a column of Amberlite IR-120 (H<sup>+</sup> form) (0.5 g). Elute **I** with H<sub>2</sub>O (100 ml) and determine by fivefold dilution and measurement of the u.v. absorption at 244 m $\mu$ . Then elute **II** with 5% HCl (100 ml) and determine by measurement of the colour developed with alkaline 1-naphthol reagent (cf. Greenberg and Lester, *J. Pharmacol.*, 1946, **88**, 87). The procedure has been applied to the determination of **I** and **II** in powders, tablets, drops and syrups, and also, with some modifications, to the determination of **I** and **II** in urine. The error is < + 3%.  
A. R. ROGERS

**4460. Determination of Largactil [chlorpromazine].** P. Spacu, E. Antonescu and C. Gheorghiu. *Rev. Chim., Acad. R.P.R.*, 1959, **4** (2), 243-252 (in English).—Four methods are described for the quant. determination of chlorpromazine (**I**) in pharmaceuticals by means of ammonium reineckate (**II**) and K reineckate (**III**). (i) For gravimetric macro-determination, take an aliquot of **I** (20 to 64 mg) and add conc. HCl (1 to 2 ml) and **III** until the ppt. becomes violet. Filter after 5 min. through a sintered-glass crucible (porosity 2 or 3) and wash the ppt. with water until free from Cl<sup>-</sup>. Dry at 120°. The factor for conversion is 0.7035. (ii) To a similar soln. of **I** add dil. acetic acid (0.5 to 1 ml) and a 1% soln. of **II** until the soln. becomes red, warm to 70°, and cool on ice. Filter as before and wash with water until the filtrate is colourless. Dry at 110°. The conversion factor is 0.4987. This method is also applicable to 0.6 to 2-mg amounts of **I** if the reaction proceeds in the cold. (iii) For the spectrophotometric determination of 0.4 to 1.8 mg of **I**, proceed as in (i) and dissolve the dry ppt. in acetone. Measure the extinction at 574 m $\mu$ . The Beer-Lambert law is obeyed. (iv) For the potentiometric titration of 21 to 55 mg of **I**, proceed as in (iii), dissolving the ppt. in acetone ( $\approx$  20 ml). Add an equal vol. of water, and titrate with 0.01 or 0.05 N AgNO<sub>3</sub> with a silver-wire electrode and a S.C.E. as reference electrode.  
M. A. ELLIS

**4461. Bromimetric estimation of methocarbamol.** P. M. Parikh and S. P. Mukherji (Zandu Chemical Works Ltd., Gokhale Road, South, Bombay 28, India). *Drug Standards*, 1960, **28** (2), 48-50.—To a soln. of the sample or a tablet extract in 20% aq. ethanol (50 ml) containing  $\approx$  0.2 g of methocarbamol (**I**) add H<sub>2</sub>O (25 ml) and 0.1 N bromine (50 ml) and cool in ice for 15 min. with occasional shaking. Add 10% KI soln. (20 ml) and CHCl<sub>3</sub> (20 ml), shake well, set aside at room temp. for 5 min. and titrate with 0.1 N Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> with starch as indicator. Perform a blank titration. The recovery of **I** is > 99.7%. Sucrose, lactose, starch, Mg stearate, talc and gum acacia do not interfere.  
A. R. ROGERS

**4462. Analytical examination of piperidinomethyl-tolylpropanone.** I. Gyenes (Kőbányai Gyógyszerárugár Gyógyszertechnol. Kutatólab., Budapest). *Magyar Kém. Foly.*, 1960, **66** (2), 55-61.—The m.p. of the HCl salt of piperidinomethyltolylpropanone (2-methyl-3-piperidino-1-*p*-tolylpropan-1-one) (**N** 553) (**I**) has been determined as a function of the rate of heating. The m.p. of its eutectic mixture with phenacetin is also a measure of its purity. The free base of **I** can be identified by its refractive index and by the equiv. wt. of its basic picrate as determined with 0.01 N HClO<sub>4</sub> in chlorobenzene-

propionic acid-propionic anhydride. The HCl salt can be identified by a colour reaction with H<sub>2</sub>SO<sub>4</sub> and formaldehyde; other colour tests are also considered. The u.v. spectrum in methanol (max. absorption at 255 m $\mu$  for the free base and 253 m $\mu$  for the HCl salt) and the i.r. spectrum are discussed. For the quant. determination of **I**, the following methods can be used—titration with 0.01 N or 0.05 N HClO<sub>4</sub> in acetic acid-acetic anhydride, in the presence of Hg<sup>II</sup> acetate; extraction with benzene and determination of the base with HClO<sub>4</sub> in anhyd. medium; potentiometric titration with 0.01 N HClO<sub>4</sub> in methyl cyanide-acetic acid-acetic anhydride (100:6.7:1.7), with Tropaeolin OO as indicator; and titration of the oxime with 0.1 N HCl in an anhyd. medium. Procedures for the quant. and semi-quant. control of the decomposition products are also recommended. All these methods are described.  
A. G. PETO

**4463. Analytical study of quinuonium sulphate (Acaprin). II. Photometric and spectral determination.** V. Špinková and J. Zýka (Dept. Anal. Chem., Charles' Univ., Prague). *Českosl. Farm.*, 1960, **9** (2), 75-78.—*Photometric determination*—To the soln. of the sample (0.1 ml) add 25% HCl (2 ml) and boil under reflux for 6 hr. After hydrolysis transfer to a 25-ml flask and dilute to vol. with H<sub>2</sub>O. Mix, and to an aliquot (0.6 ml) add 0.1% NaNO<sub>2</sub> soln. (1 ml), then after 1 min. a 0.5% soln. of ammonium sulphamate (1 ml), and after a further 1 min. a 0.3% soln. of N-(1-naphthyl)ethylenediamine hydrochloride (1 ml); dilute to 25 ml with H<sub>2</sub>O and measure the extinction of the red colour at 530 m $\mu$ . Compare with a calibration curve. *Spectral determination.* (i)—Dilute the sample soln. (0.1 ml) to 500 ml with 0.01 N HCl and measure the extinction at 274 m $\mu$ . Compare with a standard. (ii)—Dilute the sample soln. to 250 ml with 0.01 N KOH, mix, and dilute an aliquot (10 ml) to 25 ml with 0.01 N KOH. Measure the extinction at 275 m $\mu$ . Compare with a standard.  
J. ZÝKA

**4464. Polarographic determination of 5-acetamidomethyl-4-amino-2-methylpyrimidine and the sulphate of 4-amino-5-aminomethyl-2-methylpyrimidine in production samples.** M. Konupčík and O. Manoušek (Dept. Tech. Contr. Farmakon, Olomouc, Czechoslovakia). *Českosl. Farm.*, 1960, **9** (2), 78-81.—Both compounds yield well-developed polarographic waves in acid soln. or buffered soln. of pH > 9. For analytical purposes the medium of pH 4.5 to 5 (acetate buffer) is recommended; both compounds can be differentiated by derivative polarography at this pH.  
J. ZÝKA

**4465. Determination of lead in pharmaceuticals.** I. C. R. Mehta, N. V. Mankad and M. B. Devani (L.M. College of Pharm., Ahmedabad). *Indian J. Pharm.*, 1960, **22** (2), 37-38.—Samples of lead monoxide, lead acetate and conc. soln. of lead subacetate have been assayed gravimetrically as sulphate and as the salicylaldehyde complex, titrimetrically with EDTA (disodium salt) and by the methods of the U.S.P. XIV, the [U.S.] N.F. X, the B.P. 1958 and the I.P. 1955. The mean and standard deviations, based on 10 determinations, are reported for each method. The salicylaldehyde and EDTA methods are precise and give results comparable with those by the sulphate method. The N.F., B.P. and I.P. methods give low results for conc. soln. of lead subacetate.  
A. R. ROGERS

**4466. Azeotropic distillation as a method for drug control. Determination of ethanol by means of distillation of a ternary mixture ethanol - toluene - water.** B. Melichar and I. Jakubec (Pharm. Fac., Univ. Brno, Czechoslovakia). *Českosl. Farm.*, 1960, **9** (2), 72-75.—The mixture ethanol - toluene -  $H_2O$  (41.2:49.1:9.7) is better for azeotropic purposes than the mixture ethanol - benzene -  $H_2O$ , proposed in previous papers (cf. *Anal. Abstr.*, 1960, **7**, 2443). Improvements in the apparatus have been made. The described method is suitable also for use with samples containing < 20% of ethanol.

J. ZÝKA

**4467. Radiometric determination of some pharmacopoeial ointments and powders. Determination of calcium and sulphur.** M. Šaršunová, J. Tölgyessy and J. Majer (Pharm. Fac., Komenský Univ., Bratislava, Czechoslovakia). *Českosl. Farm.*, 1960, **9** (2), 68-71.—The pptn. reactions of Ca with oxalate soln., and S, after conversion into sulphate, with  $BaCl_2$  soln. were modified for radiometric measurements with radioactive calcium ( $CaCl_2$ ) and sulphur ( $H_2SO_4$ ) and the technique described previously (*Anal. Abstr.*, 1960, **7**, 2958). Results from the proposed method were in good agreement with those of gravimetric determinations.

J. ZÝKA

**4468. Proposed assay for Benzoic and Salicylic Acid Ointment U.S.P.** S. Anderson and W. J. Rost (Chem. Dept. and School of Pharmacy, Univ. of Kansas City, Mo., U.S.A.). *Drug Standards*, 1960, **28** (2), 46-48.—Dissolve the sample (3 g) in 50% aq. ethanol, dilute to 1 litre and measure the u.v. absorption at 270 and 310  $m\mu$ . At 270  $m\mu$  the values of  $E_{1\%}^{1\text{cm}}$  are—benzoic acid (I), 68-89, salicylic acid (II), 38-77; at 310  $m\mu$  the values are—I, 0.17, II, 196-3. Assays of eight samples indicated recoveries of 99.9% of I and 101.3% of II; the standard deviations were  $\pm 0.4\%$  for I and  $\pm 0.9\%$  for II.

A. R. ROGERS

**4469. Pressurised pharmaceutical aerosols for inhalation therapy. I. Physical testing methods.** I. Porush, C. G. Thiel and J. G. Young (Riker Lab., Inc., Northridge, Calif.). *J. Amer. Pharm. Ass., Sci. Ed.*, 1960, **49** (2), 70-72.—The methods used for controlling the manufacture of these aerosols are described, and results of tests for uniformity of valve delivery, particle size and pressure are reported.

**II. Analytical control methods.** J. G. Young, I. Porush, C. G. Thiel, S. Cohen and C. H. Stimmel. *Ibid.*, 1960, **49** (2), 72-74.—Procedures are described for the spectrophotometric assay of the active ingredients (adrenaline acid tartrate or isoprenaline), the amount of active ingredient delivered per dose, and the moisture content by the Karl Fischer method. The stabilities of the drugs are checked by a bioassay method, and specifications for the propellants are given.

A. R. ROGERS

**4470. Biochemical test for determination of the bactericidal power of disinfectants.** G. Friesen (Apothekende Stadt. Krankenhaus Neukölln, Berlin). *Dtsch. ApothZtg*, 1960, **100** (5), 119-121.—The disinfectant, suitably diluted, is added to cultures of putrefactive bacteria obtained by exposure to the air of a decoction of green leaves. After further incubation the cultures are treated with a 1% soln. of 2:3:5-triphenyltetrazolium chloride.

Viable bacteria are stained bright red within 25 min., while dead bacteria are unstained. A. G. COOPER

*See also Abstracts—4104. Testosterone derivatives. 4363, 4364. Determination of camphor. 4366. Determination of pyridine derivatives. 4393. Sapogenification cloud test for beeswax. 4405. Caffeine, phenazone and phenacetin in human tissue. 4417. Assay of diosgenin. 4439. Cortisol and deoxycortisol in plasma. 4479. Dyes in pharm. products. 4505. Assay of vitamin B<sub>12</sub>.*

## Food

*Food and food additives, beverages, edible oils and fats, vitamins.*

**4471. Determination of reducing sugars by means of back-titration against alkaline copper solution.** I. Masahito Takahashi (Biol. Dept., Sci. Fac., Kobe Univ., Mikage). *Bull. Chem. Soc. Japan*, 1960, **33** (2), 178-181 (in English).—A volumetric method for determining reducing sugars by titrating a boiling mixture of modified Fehling soln. (10 ml) and the sample soln. (20 ml) with a standard sugar soln. is described. The method is applicable over a wide range of sugar concn., especially dilute soln., with high accuracy.

I. JONES

**4472. Determination of the ionic calcium content of clarified cane juice.** P. Hidi and R. I. Nicholson (Res. Dept., Colonial Sugar Refining Co. Ltd., Sydney, Australia). *Int. Sugar J.*, 1960, **62**, 9-12.—The determination of ionic Ca in sugarcane juices without disturbing the equilibrium with non-ionic Ca is not possible by established methods, but can be effected by measuring the extinction of the Ca - murexide complex. *Procedure*—Clarified, filtered juice (15 ml) is placed in 2 beakers with 2 ml of 0.0015 M EDTA (disodium salt), and to one of these is added a 0.1% soln. of murexide - KCl (1:24) in 0.02 N acetate buffer (pH 6.5) (5 ml) and to the other (blank) 5 ml of the buffer alone. After being adjusted to pH 6.5 the soln. is made up to 25 ml and the extinction at 485  $m\mu$  is measured in 4-cm cells. Simultaneously 0.005 M  $CaCl_2$  (15 ml), 1 M  $CaCl_2$  (10 ml) and water (15 ml) are treated with the murexide soln., adjusted to pH 6.5 and made up to 25 ml, and their extinctions measured against water as a blank. The formation constant of the murexide complex is calculated from the water and  $CaCl_2$  samples and the Ca content can then be calculated for the juice sample. Any colour in the juice sample is compensated by the juice blank. The EDTA soln. is added to the juice to complex  $Cu^{2+}$  and  $Mn^{2+}$ , which would interfere, and a correction (one-half of the EDTA added) is made when calculating the Ca content (this cannot cause an error > 1 millimole per litre). No correction for added indicator is necessary. Iron does not interfere if a juice blank is used. Results for variously limed juices are given and discussed.

E. J. H. BIRCH

**4473. New method for the estimation of the meat-extract content of commercial extracts and cubes.** M. T. Cuzzoni and T. P. Lissi (Ist. Chim. Farm. Tossicol. Univ., Pavia, Italy). *Farmaco, Ed. Sci.*, 1960, **15** (2), 95-103.—The current low cost of creatine presents the need for an alternative to the conventional determination of creatinine as a criterion of purity of meat extracts. Paper chromatography of extract hydrolysates shows the presence of adenine and hypoxanthine in meat

extracts, of adenine and xanthine in yeast extracts, and the absence of purine bases in vegetable extracts. The hypoxanthine content found for the pure meat extracts examined was  $1.14 \pm 0.03\%$ , and this figure is proposed as a criterion of purity for meat extracts, and may be used for the estimation of meat extract in mixtures. *Procedure*—Hydrolyse the extract (5 g) for 8 hr. at  $100^\circ$  with  $N H_2SO_4$  (100 to 200 ml depending on the meat-extract content). Adjust an aliquot (25 ml) to pH 1 with NaOH, and add excess of a suspension of  $Ag_2O$ , prepared by mixing  $0.4 N AgNO_3$  (50 ml) and  $0.4 N Ba(OH)_2$  (50 ml), washing the ppt. by decantation, and suspending it in  $H_2O$  (20 ml). Set the mixture aside for 12 hr. and then centrifuge. Dissolve the purines from the ppt. by successive extraction at  $100^\circ$  for 5 min. with dil. HCl (2-ml portions), to a final volume of 10 ml. Chromatograph ( $2 \times 50 \mu$ ) by the ascending technique on Whatman No. 4 papers, with  $n$ -butanol- $H_2O$ -15 N aq.  $NH_3$  (86:14:1). The solvent front rises 25 cm in 8 hr.  $R_F$  values are, for adenine, 0.44; hypoxanthine, 0.24; xanthine, 0.17; guanine, 0.01. Locate the purine bases on one chromatogram by spraying with a 2% soln. of  $AgNO_3$ , leaving it in the dark for 5 min., then immersing in a 2.5% soln. of  $K_2CrO_4$  and washing with 0.1 N  $HNO_3$ . The purine spots are coloured red. Elute the hypoxanthine from the corresponding portion of the second chromatogram by overnight immersion in 0.1 N HCl (10 ml). Filter the extract and measure the u.v. absorption at 284  $m\mu$ . For hypoxanthine  $E_{1\%}^{1cm} = 0.795$ . Recoveries of added hypoxanthine were from 90 to 92%. Estimates of the meat-extract content of known mixtures were within  $-3\%$  of the correct figure. E. C. APLING

**4474. Extraction of milk for DDT determination. One-day complete method.** R. W. Storherr and P. A. Mills (Div. of Food, Food and Drug Admin., Dept. of Health, Education and Welfare, Washington, D.C., U.S.A.). *J. Ass. Off. Agric. Chem.*, 1960, **43** (1), 81-82.—A procedure for the extraction of DDT from milk to enable the assay to be carried out in time to withdraw contaminated supplies is described. *Procedure*—To 100 g of milk are added 5 ml of 5% K oxalate soln., 100 ml of 95% ethanol (or isopropyl alcohol), and then, with shaking, 200 ml of diethyl ether and 100 ml of light petroleum. The non-aqueous layer is filtered and the light petroleum washings of the apparatus are added. After adding 15 ml of benzene, the soln. is evaporated to dryness over a steam bath without overheating. The residue is transferred with light petroleum to a separating-funnel and extracted with methyl cyanide satd. with light petroleum ( $4 \times 25$  ml) and the combined extracts are evaporated just to dryness. The residue is chromatographed with light petroleum on a 100-mm column of activated Florisil, and aliquots of the eluate are used for paper chromatography, and for the colorimetric determination of DDT. E. J. H. BIRCH

**4475. Investigation and estimation of the radioactive isotopes strontium-89 and strontium-90 in dried milk.** L. Jeanmaire and G. Michon. *Lait*, 1959, **39**, 369-380.—Dried milk is ashed and the alkaline-earth metals are pptd. Strontium is separated from calcium by taking advantage of the insolubility of  $Sr(NO_3)_2$  in conc.  $HNO_3$ , and is purified on a cation-exchange resin. The radioactivity due to  $^{89}Sr$  and  $^{90}Sr$  is then measured. Strontium-90 disintegrates to give  $^{90}Y$ , which is separated as the oxalate, and from the determination

of its radioactivity the amount of  $^{90}Sr$  originally present can be calculated. NUTR. ABSTR. REV.

**4476. Examination of casein preparations by paper electrophoresis.** M. T. Sode-Mogensen and E. Lahav (Dept. Dairy Chem. and Bact., Royal Vet. and Agric. College, Denmark). *Lab. Practice*, 1960, **9** (1), 21-28, 34.—A routine procedure for the electrophoretic separation of  $\alpha$ -,  $\beta$ - and  $\gamma$ -casein and the effects of variations from the standard procedure are described. *Procedure*—Mix casein (5 g on dry basis) with water (20 ml) and add 0.1 N NaOH (30 ml), with vigorous stirring. Finally, add barbitone buffer (pH 8.6) (20 ml) and dilute to 100 ml. Apply the casein soln. (0.03 ml) to strips ( $4 cm \times 42.5 cm$ ) of Whatman 3 MM paper, previously soaked in barbitone buffer (pH 8.6,  $\mu = 0.1$ ), drained and equilibrated for 2 hr. Apply a constant potential (4.7 V per cm, 0.25 to 0.30 mA per cm of paper width) for 16 hr. at  $4^\circ$ . On completion of the run, cut away the wet ends of the paper and dry at  $110^\circ$  for 30 min., treat with Naphthalene black 12 B (C.I. Acid Black 1) for 10 min., rinse with a soln. containing methanol (45 g), water (45 g) and glacial acetic acid (10 g), and air-dry at  $20^\circ$ . Make the papers transparent by treatment for 30 min. with a mixture of 1-bromonaphthalene and liquid paraffin (1:1, by wt.), blot dry and scan in a densitometer, with a green NO OGR 1 filter. Variations in pH, ionic strength and temperature from those described result in inferior separations. E. C. APLING

**4477. Determination of the odour value of Mexican garlic.** N. Alfonso and E. Lopez (Inst. Mex. de Invest. Tecnol., Mexico D.F., Mexico). *Z. Lebensmittelforsch.*, 1960, **111** (5), 410-413.—The odour of garlic is evaluated by determination of the pyruvic acid formed when alliin, the parent substance of the odouriferous principle, alliin, is broken down by the natural enzyme of the plant. A weighed amount of garlic (50 g) is ground up with a weighed 100 g of water in an electric mixer for 3 min. at a temp. from  $22^\circ$  to  $37^\circ$  (cooling if necessary). After standing for 2 min., the suspension is mixed well and 10 ml is withdrawn by a pipette with wide opening and transferred to a measured 60 ml of 15% trichloroacetic acid soln. in a 100-ml flask. The amount of suspension added is given by the diminution in weight of the main bulk. The contents of the flask are well mixed, then made up to 100 ml with trichloroacetic acid soln., and filtered through Whatman No. 42 paper. The filtrate (20 ml) is shaken with 2:4-dinitrophenylhydrazine in 2 N HCl and left for 1 hr. The hydrazone formed is shaken out with 40, 20 and 10 ml of ethyl acetate and the combined extracts are extracted twice with 50 ml of 2 N aq.  $NH_3$ . The combined ammoniacal extracts are extracted with 10 ml of ethyl acetate and allowed to stand for 40 min. The extinction of the ammoniacal soln. is determined at 370  $m\mu$  against 2 N aq.  $NH_3$  as standard, and the pyruvic acid estimated from the calibration curve for its 2:4-dinitrophenylhydrazone. The factor for conversion of pyruvic acid to alliin is 2.0113 and to alliin, 1.8409. C. L. HINTON

**4478. Methods for the analysis of vanilla extracts for resins, carbonyl compounds, amino acids and other organic acids.** E. A. Prill, C. A. Porter, R. C. Staples and H. P. Burchfield (Boyce Thompson Inst. for Plant Res., Inc., Yonkers, N.Y., U.S.A.). *J. Ass. Off. Agric. Chem.*, 1960, **43** (1), 96-107.—A systematic scheme of analysis is described.



**Procedure (i) for gums**—To 100 ml of the extract containing 35% ethanol is added 225 ml of abs. ethanol and the pptd. gums are centrifuged off and weighed. **(ii) Vanilla resins**—The combined supernatant liquid and washings from the gum determination are evaporated in a vacuum rotary evaporator with the addition of  $H_2O$  and the solvent is recovered. The suspension of resins obtained is adjusted to pH 2 and centrifuged. The proportions of the resin sol. in tetrahydrofuran, methanol and dil. aq.  $NH_3$  (1:9), respectively, are determined gravimetrically. The i.r. spectrum of the resins sol. in tetrahydrofuran is examined. **(iii) Carbonyl compounds**—The resin-free filtrate is treated with 0.8 g of 2,4-dinitrophenylhydrazine and 3 ml of dichloromethane, and the hydrazone obtained is determined gravimetrically. Carbonyl compounds in the recovered solvent are similarly determined. **(iv) Amino acids**—The filtrate from (iii) is treated with 0.4 N  $Ba(OH)_2$  to remove sulphate and evaporated to a syrup, and then mixed with 80% ethanol and filtered if necessary. The amino acids are retained on a Dowex 50-X8 column ( $H^+$  form) and eluted with 60 ml of 2 N HCl; total amino acids are determined colorimetrically with ninhydrin at 570  $m\mu$ , and individual amino acids are separated by two-dimensional paper chromatography. **(v) Other organic acids**—These are determined by retention on Dowex 1-X10 (formate form) and gradient elution with formic acid. The fractions obtained are evaporated to remove formic acid and titrated with 0.01 N NaOH. The results for 6 commercial samples and 8 authentic extracts are compared and discussed. E. J. H. BIRCH

**4479. Application of chromatography to the investigation of colouring matters in foods, beverages and pharmaceutical products.** H. S. Dellinger (Fac. Quím. y Farm., Univ. Chile). *An. Bromatologia*, 1960, **12** (1), 9-18.—The dyes are extracted from solid materials by maceration for 24 hr. with 70% ethanol containing 5% of aq.  $NH_3$ ; protein-containing materials may require treatment with pepsin or papain. They may then be separated (i) by extraction with amyl alcohol at pH 1; (ii) by extraction with quinoline and re-extraction into water (Mottier and Poterat, *Mitt. Lebensmitt. Hyg., Bern*, 1953, **49**, 293); (iii) by a double separation on wool (Thaler and Sommer, *Z. Lebensmitt.-Untersuch.*, 1953, **97**, 441); these three methods extract only acid dyes; (iv) by adsorption on  $Al_2O_3$ . In this method, acid dyes may be adsorbed from a soln. (10 ml) acidified with acetic acid (2 drops) and eluted with 1% aq.  $NH_3$  soln., or from a soln. neutralised to pH 7 and eluted with water. The former procedure extracts more dye, but by the latter procedure the dyes retain their original colour. Basic dyes are adsorbed on  $Al_2O_3$  that has been treated with 1% ethanolic tannin soln. and dried, and are eluted with 95% ethanol. Fat-soluble dyes are extracted with light petroleum, adsorbed on  $Al_2O_3$ , and eluted with benzene-petroleum spirit. For chromatography on Whatman No. 1 or S. & S. 2043b paper, acid and basic dyes are developed with 2% of Na citrate in 5% aq.  $NH_3$  soln., and fat-soluble dyes with methanol-acetic acid (19:1);  $R_F$  values and colour reactions are tabulated for a number of natural and synthetic colouring matters. L. G. L. UNSTEAD-JOSS

**4480. New method for extracting, concentrating and purifying synthetic acid water-soluble dyes in foods and beverages.** H. S. Dellinger (Fac. Quím. y Farm., Univ. Chile). *An. Bromatologia*, 1960, **12**

(1), 113-115.—Certain substances (e.g., sugars, organic acids and mucilages) present in confectionery and alcoholic beverages interfere with the adsorption of acid dyes on  $Al_2O_3$ . They may be removed by treatment with an ion-exchange resin; pastilles, etc., are first dissolved in 20 ml of  $H_2O$ . The coloured soln. is passed through a column containing 15 to 20 g of resin (Merck, No. 1) and the percolate is treated with 1 drop of acetic acid and shaken with 5 g of  $Al_2O_3$ . If the supernatant liquid is not colourless, the treatment with acetic acid and  $Al_2O_3$  is repeated. The coloured  $Al_2O_3$  is washed twice with  $H_2O$  and once with 95% ethanol and dried, and the colour is extracted with 20 ml of  $H_2O$  containing 1 drop of 5% aq.  $NH_3$  soln. The extract is then examined by paper chromatography. L. G. L. UNSTEAD-JOSS

**4481. Polarographic method for determining nitrite in meat-curing brines.** J. H. Dhont (Central Inst. for Nutrition and Food Res., T.N.O., Utrecht, The Netherlands). *Analyst*, 1960, **85**, 144-146.—The sample with 0.2 ml of saturated Na acetate soln. is heated in a boiling-water bath for 30 min., then cooled and adjusted to 50 ml and filtered. A 2-ml aliquot of the filtrate is added to each of two flasks and a standard soln. of  $NaNO_2$  is added to one. With the flasks in ice-water a 2-naphthol reagent (prep. described) and dil. HCl are added to each. After 1 hr., 5 ml of ethanol and 1 ml of aq.  $NH_3$  are added and the liquids are diluted to 10 ml. A polarogram of each soln. is recorded between 0.1 and -0.5 V against the mercury-pool anode, and the diffusion current is corrected for the reagent blank value. The concn. of nitrite in the sample is calculated from the increase in diffusion current caused by the addition of standard soln. Slight modifications of the method for low concn. of  $NaNO_2$  and for pump brines are described. The lower limit of the method is 0.0075%. Recovery of known amounts ranged from 97.5 to 102%. A. O. JONES

**4482. Rapid method for the determination of the protein content of barley.** T.-M. Enari, M. Nummi and J. Mikola (Panimolaboratorio-Lab. for Brewing, Helsinki, Finland). *Brauwissenschaft*, 1960, **13** (3), 91-92.—The finely ground sample (1 g) is shaken for 45 min. with 0.005 N NaOH (100 ml). The protein (as distinct from the total N) in the filtered extract (1 ml) is determined by measuring at 540  $m\mu$  the turbidity produced with sulphosalicylic acid according to the method of Feinstein and Hart (*Anal. Abstr.*, 1959, **6**, 4955). The results agree well with those obtained by the Kjeldahl method; the standard deviation is equiv. to  $\pm 0.1\%$  of protein (14 determinations). P. S. ARUP

**4483. Quantitative determination of carbohydrates in malt extracts.** C. Sampietro and I. Invernizzi (Lab. Chim. Provinciali di Igiene, Como, Italy). *Nahrung*, 1959, **3** (11-12), 1065-1074 (in German).—A method for the separation and determination of maltose, glucose, sucrose and dextrin is presented. Maltose and glucose require three determinations, viz. copper reduction by Lane and Eynon's method (*J. Soc. Chem. Ind., London*, 1923, **42**, 32r) and measurement of the optical rotation before and after heating with  $CaO$  at 80°; sucrose is determined in a separate aliquot by heating under reflux with 20% citric acid soln. for 8 min. and determining reducing sugar as before; dextrin is hydrolysed with HCl ( $d = 1.125$ ) for 3 hr. and

the reducing sugar is determined as before. The procedures and methods of calculation are described.

B. HEINING

**4484. Contribution to the analysis of hops.** G. Krauss, A. Rebmann and H. Egner (Brauerei Rob. Leicht A.-G., Stuttgart-Vaihingen, Germany). *Brauwissenschaft*, 1960, **13** (2), 42-45.—Differences of  $\geq 0.3\%$  are found between the results for  $\alpha$ -acids in fresh hops (20 samples) and in hops heated at  $90^\circ$  (2 samples) as determined by the Wöllmer (gravimetric), conductimetric (Trolle and Djurtott modification) and spectrophotometric methods. The standard deviation of the difference of the physical from the gravimetric results is  $\pm 0.15$ . The spectrophotometric results were obtained by a modification (described here) of the Alderton procedure by Gimbel *et al.* (*Anal. Abstr.*, 1960, **7**, 2982). The Wöllmer method proved unsatisfactory when a sample which had been heated at  $90^\circ$  for 4 hr. was analysed; the results given by the two physical methods were satisfactory and concordant.

P. S. ARUP

**4485. Simplification and shortening of analysis of hop concentrates.** W. Kleber, G. Franke and P. Schmid (Wissenschaftl. Stat. f. Brauerei, Munich). *Brauwissenschaft*, 1960, **13** (2), 38-39.—An ethereal soln. of the hop bitters, free from tannins, is obtained by vigorously shaking the sample (1 l to 1.5 g) under  $\text{CO}_2$  with water (200 ml) and diethyl ether (4 to  $5 \times 50$  ml) for 5 min. until the ether layer remains colourless. The duration of the later extractions can be shortened. The combined ether extracts (washed with water and dried over  $\text{CaCl}_2$ ) are evaporated to dryness under reduced pressure and under  $\text{CO}_2$ . A soln. of the residue in methanol is then analysed according to the Wöllmer procedure. The results for  $\alpha$ -acids are consistently slightly higher than those obtained by the Schild and Riedel extraction method (*Ibid.*, 1951, **4**, 21).

P. S. ARUP

**4486. Conductimetric titration of isohumulone in beer according to Verzele.** H. Egner (Brauerei Rob. Leicht A.-G., Stuttgart-Vaihingen, Germany). *Brauwissenschaft*, 1960, **13** (2), 31-32.—The method (Wallerstein Labs Commun., 1959, **22**, 173) gives results in good agreement with those obtained by the Klopfer method (*Ibid.*, 1957, **20**, 109) and, although more laborious, can be recommended for use when a spectrophotometer is not available.

P. S. ARUP

**4487. Detection of [traces of] quaternary ammonium compounds.** W. Kleber, M. Lindemann and G. Franke (Wissenschaftl. Stat. f. Brauerei, Munich). *Brauwissenschaft*, 1960, **13** (2), 39-40.—Improved chromatograms are obtained by applying the following modifications to the Garcia and Couerbe procedure (*Anal. Abstr.*, 1957, **4**, 2368). A slowly moving descending solvent composed of butanol-pyridine-water (6:4:3) is used on paper cut into wedge-shaped strips with the pointed ends downwards. After development for 20 hr., the chromatograms are dried, sprayed with 0.5% (instead of 5%)  $\text{Na}_2\text{CO}_3$  soln., and again dried. A spraying with a soln. of bromophenol blue (0.02%) colours the spots blue on violet. The spots are intensified by heating at  $100^\circ$  for 5 min.

P. S. ARUP

**4488. Paper-chromatographic separation and determination of glycerol in wines and liqueurs.** K. G. Bergner and H. Meyer (Chem. Landesuntersuchungsamt., Stuttgart, Germany). *Dtsch. Lebensmitt.*

*Rdsch.*, 1960, **56** (2), 49-52.—Glycerol may be determined in wine after ascending paper chromatography with water-saturated *n*-butanol-*n*-propanol (4:1) as mobile phase, at a temp. of  $40^\circ$  to  $44^\circ$ . Spots are located by treatment of a parallel chromatogram of wine plus glycerol with ammoniacal  $\text{AgNO}_3$  soln. at  $105^\circ$ . For the determination, the relevant areas are cut from the paper and the glycerol is extracted with water and oxidised with periodate. The resulting formaldehyde is determined by the chromotropic acid reaction after removal of excess of periodate and iodates by treatment with arsenious acid and  $\text{Ag}_2\text{SO}_4$ . Amounts of 5 to  $150 \mu\text{g}$  of glycerol can be satisfactorily determined in 0.005 to 0.01 ml of wine.

E. C. APLING

**4489. Determination of iron in wine using 2:4:6-tripyridyl-sym.-triazine.** P. Collins and H. Diehl (Chem. Dept., State Univ., Ames, Iowa, U.S.A.). *Anal. Chim. Acta*, 1960, **22** (2), 125-127.—2:4:6-Tripyridyl-sym.-triazine (I) has been used instead of bathophenanthroline or 1:10-phenanthroline (II) without preliminary wet-ashing. Comparison of the results obtained by the direct I method and by wet-ashing followed by the use of either II or I shows the results obtained by the direct method to be reproducibly low. It is suggested that 'complexed iron' is responsible for the difference between the direct and the wet-ash results, and that the 'uncomplexed iron' determined by the direct method is that which is active in forming wine turbidity. Replacing II with I in the wet-ash procedure allows smaller samples to be used and makes the removal of excess of perchloric acid unnecessary.

E. G. CUMMINS

**4490. Determination of copper in water-alcohol mixtures and spirits.** II. A. Popoff (Chem. Inst., Bulgarische Akad. d. Wissenschaften, Sofia). *Nahrung*, 1959, **3** (11-12), 1079-1085 (in German).—*Procedure*—Pass 100 ml of sample through a column (5 cm  $\times$  1 cm) of Wofatit F at the rate of 100 ml per hr. Wash with 10 to 20 ml of Cu-free ethanol and elute the Cu with 10 ml of 10% HCl (1 ml per min.) followed by 30 ml of 1% HCl and 20 ml of water; make the combined eluate and washings up to 100 ml with water. Transfer 3 ml (5 to 60  $\mu\text{g}$  of Cu per ml) to a 50-ml flask, add 10 ml of buffer (100 g of ammonium acetate dissolved in 100 ml of water) and dilute to 49 ml with water; add 0.5 ml of 0.1% dithio-oxamide soln. in 96% ethanol and make up to the mark; shake and measure the extinction with a red filter. Determinations of 5 to 60 mg of Cu per litre gave coeff. of variation of 3 to 4%. The method described is applicable to coloured soln.

B. HEINING

**4491. Chromatography of sterols and its application to the detection of animal and vegetable fats in the presence of each other.** J. W. C. Peereboom and J. R. Roos (Reichsuntersuchungsanst. f. Molkereiprod. u. Nahrungsfette, Leiden, Holland). *Fette, Seif., Anstrichmitt.*, 1960, **62** (2), 91-100.—The fat mixture is hydrolysed and the sterols are isolated by the method of Den Herder (*Neth. Milk Dairy J.*, 1955, **9**, 261). Cholesterol is then separated from the phytosterols by paper chromatography by the zone separation method. The paper (S. & S. 2043b Mgl) is impregnated with liquid paraffin in light petroleum. Development is carried out at  $22^\circ$  to  $24^\circ$  for 40 to 45 hr. with 84% acetic acid. Several spotting agents are discussed. By this method very small amounts of

animal and/or vegetable fats can be detected or determined in mixtures. Determination of the arachidonic acid content of mixtures is also discussed; because this acid occurs in small amounts in animal fats, but is absent from vegetable oils, or is present in them in traces only, this is a further method for the estimation of animal fats in vegetable fats. All these methods are described in detail.

A. G. PETO

**4492. Quantitative fatty-acid analysis of vegetable oils by gas-liquid chromatography.** B. M. Craig and N. L. Murty (Prairie Reg. Lab., Saskatoon, Saskatchewan, Canada). *J. Amer. Oil Chem. Soc.*, 1959, **36** (11), 549-552.—The fatty-acid compositions of six vegetable oils and two synthetic mixtures were determined by gas chromatography and compared with spectrographic data. The iodine values calculated from the gas-chromatographic results were in good agreement with the measured iodine values and the results by this method were accurate to within 1%. The best resolution of the mixtures tested is obtained with a succinic acid-diethylene glycol polyester column, but in the presence of rape-seed oil it is necessary to use an adipic acid-diethylene glycol polyester column. Stability of polyester polymers is improved by using butane-1:4-diol instead of diethylene glycol.

C. A. BLAU

**4493. Method for the quantitative paper-chromatographic determination of fatty acids by means of the copper-tetraethylthiuram disulphide complex.** M. Novák and V. Hromádková (Biochem. Dept., Food Res. Inst., Praha-Krč, Czechoslovakia). *Nahrung*, 1959, **3** (11-12), 1060-1064 (in German).—The method is based on the conversion of the fatty acids into copper salts. After chromatographic separation the spots are immersed in a 0.5% soln. of  $\text{CuSO}_4$  in 0.05% Na acetate soln. for 2 min., washed and dried. The spots are cut out, transferred to flasks, and covered with 20 ml of water and 5 ml of  $\text{N HCl}$ ; after setting aside for 10 min. with frequent shaking 10 ml of 0.01 *M* tetraethylthiuram disulphide in benzyl alcohol is added, and the extinction is measured after 30 min. at 420  $\text{m}\mu$ . The calibration curve is linear for 20 to 60  $\mu\text{g}$  of Cu.

B. HEINING

**4494. Separation of higher fatty acids from erucic acid by paper chromatography.** A. Z. Budzyński and Z. J. Zubrzycki (Health Dept., Inst. of Nuclear Res., Warsaw). *Chem. Anal., Warsaw*, 1959, **4** (5-6), 903-908.—Reversed-phase paper chromatography was applied to separate erucic acid from a mixture of saturated and unsaturated fatty acids. Kerosine was used as the stationary phase and 96% acetic acid as the mobile phase. The separation was carried out for 18 hr. at room temp. in an atmosphere of  $\text{N}_2$ . The spots were located by forming the  $\text{Cu}$  salts and converting them into  $\text{Cu}_2\text{Fe}(\text{CN})_6$ . Results for the separation of erucic acid from linseed and rape-seed oil hydrolysates are given. The method is simple and suitable for the routine analysis of fatty-acid mixtures.

L. SMAKOWSKI

**4495. Determination of conjugated *cis-trans* and *trans-trans* methyl octadecadienoates by infra-red spectrometry.** J. R. Chipault and J. M. Hawkins (Hormel Inst., Univ. Minnesota, Austin). *J. Amer. Oil Chem. Soc.*, 1959, **36** (11), 535-539.—The i.r. curves in  $\text{CS}_2$  soln. show that the *cis-trans* compounds have peaks at 10.55 and 10.16  $\text{m}\mu$  and the *trans-trans* compounds have a peak at

10.11  $\mu$ . *Cis-trans* compounds alone or in the presence of *trans-trans* conjugation may be determined directly from the extinction at 10.55  $\mu$ . In the absence of *cis-trans* isomers, conjugated *trans-trans* isomers may be determined from the extinction at 10.11  $\mu$ , but when both isomers are present a correction must be applied for the contribution of the 10.11- $\mu$  absorption of the *trans-trans* isomer.

C. A. BLAU

**4496. Estimation of the biological potency of vitamin-A sources from their maleic values.** S. R. Ames and R. W. Lehman (Res. Lab., Distillation Products Industries Div., Eastman Kodak Co., Rochester, N.Y., U.S.A.). *J. Ass. Off. Agric. Chem.*, 1960, **43** (1), 21-25.—The biological potency of vitamin-A preparations may be measured by the  $\text{SbCl}_3$  procedure before and after treatment with maleic anhydride; only those isomers in which the 2:3 and 4:5 double bonds are both *trans* react. *Procedure*—The sample (0.25 to 1 g) is saponified with ethanol-KOH and extracted with ethyl ether. The ether extract is washed and dried with  $\text{Na}_2\text{SO}_4$  and made up to 250 ml with ether. An aliquot (10 ml) is evaporated to 2 ml and then to dryness in a stream of  $\text{N}_2$  and the residue is dissolved in  $\text{CHCl}_3$  and treated with 10 ml of  $\text{SbCl}_3$  soln. (113.4 g of  $\text{SbCl}_3$  in 500 ml of  $\text{CHCl}_3$ ). The extinction is determined at 620  $\text{m}\mu$  within a few seconds after mixing. A calibration curve is obtained similarly. For the maleic value ( $m$ ) a second aliquot of the extract is evaporated, and the residue is dissolved in benzene so that 5 ml contains  $\approx 1250$  units of vitamin A. Aliquots (5 ml) are transferred to two 10-ml flasks and made up to vol. with benzene for the blank and with 10% maleic anhydride soln. in benzene for the test. The flasks are shaken and set aside for 16 hr. at 25° (time and temp. are critical). The soln. are then diluted with  $\text{CHCl}_3$  to appropriate vol. and assayed with  $\text{SbCl}_3$ . Then  $m = 100 \times (R - 1.1)/88.4$ , where  $R$  is the % recovery after reaction with maleic anhydride. The relative biopotency ( $RB$ ) is  $99.5 - 0.2m - 0.051m^2 + 0.000768m^3$ . The "estimated biopotency" ( $\mu\text{g}$ ) is given by multiplying the "blue-colour potency" ( $\mu\text{g}$ ) by 0.01  $RB$ . Results for six prep. agree well with those by bio-assay.

E. J. H. BIRCH

**4497. Vitamin A in oleomargarine.** L. Friedman (Food and Drug Admin., Dept. of Health, Education and Welfare, Washington, D.C., U.S.A.). *J. Ass. Off. Agric. Chem.*, 1960, **43** (1), 6-14.—A report of a collaborative study of a procedure for determining carotene and total vitamin A in margarine is presented. *Procedure*—Margarine (10 g) is saponified with a mixture of 75 ml of 95% ethanol and 25 ml of 50% KOH soln., by boiling for 5 min. and cooling slowly for 20 min. The soln. and rinsings of the beaker are extracted with several portions of ethyl ether. The ether layer is washed with water and dil. alkali and after drying with  $\text{Na}_2\text{SO}_4$  the extract is evaporated on a water bath until droplets of oil are formed;  $\text{N}_2$  is passed through the material for 1 min., and it is then dissolved in light petroleum and made up to 10 ml. An aliquot (5 ml) is chromatographed on a column (12 mm  $\times$  9 cm) containing from the top downwards, 4 cm of standardised alumina [adsorption index, determined with F & D Yellow No. 4 (C.I. Food Yellow 11), 30 to 40], 2 cm of alkaline alumina (adsorption index 7 to 12) and 1 cm of standardised alumina. The column is eluted with a 16% soln. of ethyl ether in light petroleum, and the carotene

fraction (traced by its colour) and the vitamin A fraction (traced by its fluorescence) are collected separately. If the vitamin A eluate is coloured it must be re-chromatographed on a magnesia - Celite (1:1) column 4 cm deep (adsorption index 20 to 35), and vitamin A is eluted from the column with 0.5% of ethanol in light petroleum. The carotene is dissolved in light petroleum and determined spectrophotometrically at 450 m $\mu$  and vitamin A is dissolved in abs. ethanol and the extinction measured at 310 and 325 m $\mu$ . It is suggested that the results should be suspect if the extinction at 310 m $\mu$  is > that at 325 m $\mu$ . The confidence interval for a single determination is  $\pm 12\%$  (95% probability).  
E. J. H. BIRCH

**4498. Experience with an extraction method for thiamine.** M. J. Deutsch, S. S. Schiaffino and H. W. Loy (Food and Drug Admin., Dept. of Health, Education and Welfare, Washington, D.C., U.S.A.). *J. Ass. Off. Agric. Chem.*, 1960, **43** (1), 55-57.—The official methods for the extraction of thiamine from preparations containing adsorbents are found to be unsatisfactory. It is recommended that a 25% soln. of KCl in 0.1 N HCl should be used for the extraction, so as to give a soln. containing  $> 50$  mg of thiamine hydrochloride per ml, which, after autoclaving for 30 min. at 120° to 123°, must have a pH  $> 3.5$ . Oxidation to thiochrome is effected as in the official method, except that the medium is satd. with NaCl or KCl. Results are compared with those obtained by the official method for 25 preparations. It is pointed out that the presence of adsorbents may also hinder the utilisation of the vitamin by the body.  
E. J. H. BIRCH

**4499. Determination of thiamine in enriched cereal and bakery products.** L. H. McRoberts (Food and Drug Admin., Dept. of Health, Education and Welfare, San Francisco, Calif., U.S.A.). *J. Ass. Off. Agric. Chem.*, 1960, **43** (1), 47-54.—A collaborative study is reported of the determination of thiamine in cereal products by the bread method (*Ibid.*, 1958, **41**, 60) and the flour method ("AOAC Official Methods of Analysis," 8th Ed., 1955, 38.22-38.28) with a comparison between the use of a direct standard and a procedural standard, and between blanks established by quenching the thiochrome fluorescence in the sample tube with HCl, or by using plain NaOH in the preparation of a separate blank tube. It is concluded that a procedural standard is not necessary except as an occasional check. The two methods of blank determination show no appreciable difference, but the HCl method is more rapid. Changes and alternatives in the official methods are recommended, including the substitution of 0.1 N HCl for 0.1 N H<sub>2</sub>SO<sub>4</sub>.  
E. J. H. BIRCH

**4500. Stability and determination of thiamine in a corn-meal enrichment mixture.** M. J. Deutsch, S. S. Schiaffino and H. C. Pillsbury (Div. of Nutrition, Food and Drug Admin., U.S. Dept. of Health, Education and Welfare, Washington, D.C., U.S.A.). *J. Ass. Off. Agric. Chem.*, 1960, **43** (1), 45-46.—The application of the AOAC method ("Official Methods of Analysis," 8th Ed., 1955, 819) for the assay of thiamine in a corn-meal enrichment mixture containing metallic iron powder, monocalcium phosphate, niacin, limestone, riboflavin and talc, leads to difficulties in the extraction procedure, and the pH rises after autoclaving. The use of HCl instead of H<sub>2</sub>SO<sub>4</sub> and pre-determination of the amount of acid required to keep the mixture acid, was studied, and

the optimum conditions for extraction were determined. *Procedure*—The sample (4.54 g) is treated with 400 ml of 0.4 N HCl, swirled for 5 min. and set aside for 10 min. at room temp. The soln. is diluted to contain  $\approx 0.2$   $\mu$ g of thiamine per ml and the determination is completed by the standard method. Analyses carried out by this method after storage of the dry mixture in unstoppered, but covered, flasks for 1 to 12 months showed that atmospheric humidity had no effect on the thiamine content.  
E. J. H. BIRCH

**4501. Extraction method for adsorbed riboflavin.** M. J. Deutsch, H. C. Pillsbury, S. S. Schiaffino and H. W. Loy (Div. of Nutrition, Food and Drug Admin., U.S. Dept. of Health, Education and Welfare, Washington, D.C., U.S.A.). *J. Ass. Off. Agric. Chem.*, 1960, **43** (1), 42-43.—Low results for riboflavin by the AOAC method ("Official Methods of Analysis," 8th Ed., 1955) are obtained when vitamins have been incorporated into the prep. on an adsorbent. The official method is modified in such cases by extracting with methanol-pyridine-water-glacial acetic acid (30:10:10:1) instead of HCl. The vol. (ml) of extraction soln. is  $< 10 \times$  dry wt. (g) of sample and the mixture is heated under reflux for 1 hr. The resulting soln. should contain  $> 0.1$  mg of riboflavin per ml.  
E. J. H. BIRCH

**4502. Chromatographic separation of vitamin-B<sub>6</sub> components in food extracts.** E. W. Toepfer, M. J. MacArthur and J. Lehman (Inst. of Home Economics, U.S. Dept. of Agric., Washington, D.C.). *J. Ass. Off. Agric. Chem.*, 1960, **43** (1), 57-59.—Samples of 1 g of various foodstuffs are extracted with 0.055 N HCl for 5 hr. in an autoclave at 15 lb; 2 N HCl gives the same results, but 20% HCl leads to loss of the pyridoxal component. The extract is adjusted to pH 4.5, and aliquots are chromatographed on ion-exchange columns. The eluted fractions are determined microbiologically with *Saccharomyces carlsbergensis*. Of the three components (pyridoxol, pyridoxal and pyridoxamine), passage through a column of Permutit H-70 at pH 7 leads to retention of pyridoxamine, which can be eluted with 20 ml of hot 0.5 N HCl. All three components are retained by a Dowex AG 50W-X8 column at pH 4.5 (though a small loss, averaging 2%, but rising to 8% with large amounts of vitamin, occurs). Pyridoxal is removed from the column with 80 ml of hot 0.05 M K acetate at pH 5.5, pyridoxol with 80 ml of hot 0.05 M K acetate at pH 6.1, and pyridoxamine with 30 ml of hot 0.2 M K citrate. The growth of the yeast, after incubation at 30° for 22 hr., was determined spectrophotometrically at 550 m $\mu$  against inoculated blanks. Pyridoxamine was the most abundant of the B<sub>6</sub> components in yeast, pyridoxal in milk solids and beef, and pyridoxol in peanut butter.  
E. J. H. BIRCH

**4503. Modification of the Atkin method for vitamin B<sub>6</sub> assay.** N. A. Hurley (Gerber Products Co., Oakland, Calif., U.S.A.). *J. Ass. Off. Agric. Chem.*, 1960, **43** (1), 43-45.—The assay of vitamin B<sub>6</sub> by culture of *Saccharomyces carlsbergensis* (ATCC 9080) according to Atkin *et al.* (*Ind. Eng. Chem.*, 1943, **15**, 141) is modified by the substitution of Vitamin-free Yeast Base (Difco), supplemented with biotin, Ca pantothenate, inositol, thiamine and nicotinic acid, for the casein hydrolysate culture medium used by Atkin. The calibration curves afforded by the two media are compared, and are



little different, so that the advantages of the new medium are convenience and uniformity.

E. J. H. BIRCH

**4504. Microbiological assay for total pantothenic acid.** E. W. Toefer (Human Nutr. Res. Div., Agric. Res. Service, U.S. Dept. of Agric., Beltsville, Md.). *J. Ass. Off. Agric. Chem.*, 1960, **43** (1), 28-29.—Results of the determination of bound pantothenic acid by the use of prepared pigeon-liver enzyme and intestinal phosphatase (Toefer *et al.*, *Ibid.*, 1954, **37**, 182) show that loss of enzyme activity renders the results unreliable. The results of 4 collaborators in an attempt to standardise the pigeon-liver enzyme by the release of pantothenic acid from yeast are reported. The results have not provided a stable standard by which the enzyme activity can be determined.

E. J. H. BIRCH

**4505. Determination of vitamin B<sub>12</sub> by the plate-diffusion method.** M. G. Golysheva and M. Yu. Rabayeva. *Trudy Vses. Nauch. Vitamin. Inst.*, 1959, **6**, 281-285; *Ref. Zhur., Khim., Biol. Khim.*, 1960, (6), Abstr. No. 7293.—Procedure—Autoclave the test material (pH 5.0) at 0.5 atm. for 15 to 20 min. or heat it on a boiling-water bath. Add NaNO<sub>2</sub> or NaCN to stabilise vitamin B<sub>12</sub> (I) and make the test soln. up to the original vol. with Na citrate soln. Introduce the test or standard soln. (> 0.1 ml) into small glass cylinders (diam. 8 mm) placed on a Petri dish inoculated with *Escherichia coli* 113-3 and incubate at 37° for 18 to 20 hr. Measure growth with a planimeter and calculate the concn. of I from a calibration curve. It is possible to determine up to 0.1 µg of I per ml. The results of the plate-diffusion method and the assay method do not differ by more than + 0.07 to - 0.03 µg of I per ml.

K. R. C.

**4506. Studies on vitamin E. I. The determination of tocopherols in animal tissues.** E. E. Edwin, A. T. Diplock, J. Bunyan and J. Green (Walton Oaks Exp. Sta., Vitamins Ltd., Tadworth, Surrey, England). *Biochem. J.*, 1960, **75** (3), 450-456.—The tissues (pig and rat muscle, rat liver and kidney) are ground with solid CO<sub>2</sub> and acetone at - 70°, and then extracted with acetone in a Soxhlet apparatus. The extract is analysed for tocopherols by the Emmerie-Engel colorimetric method after a purification process that includes saponification, removal of sterols, chromatography on florisil earth and two-dimensional paper chromatography. This last separation is essential to remove very large amounts of non-tocopherol reducing substances which are present in the tissues, and which otherwise would be determined by the Emmerie-Engel method. The molybdophosphoric acid method is unsuitable for the analysis of tocopherols in crude extracts of animal tissues, and the dangers involved in its use, particularly for the determination in serum, are stressed.

J. N. ASHLEY

**4507. Polarographic determination of tocopherols in vegetable oils.** V. I. Koltunova. *Trudy Vses. Nauch. Vitamin. Inst.*, 1959, **6**, 260-265; *Ref. Zhur., Khim., Biol. Khim.*, 1960, (4), Abstr. No. 4290.—This is a modification of Knobloch's method (*Ref. Zhur., Khim.*, 1954, Abstr. No. 14,676). Saponify the oil (3 to 5 g) with 2 N methanolic KOH (25 ml) for 30 min. in an atmosphere of N<sub>2</sub>. Add H<sub>2</sub>O (25 ml) to the mixture and then extract the unsaponified fraction with ether. Wash, dry, and evaporate the solvents from the combined ether extracts. Dissolve the unsaponified fraction in ethanol and

precipitate the sterols with an ethanolic digitonin soln. Filter, and oxidise the tocopherols in the filtrate with 0.1 N ethanolic cerium nitrate soln. (5 ml). After 10 min. extract with ether, wash the ether extract, dry, and distil off the solvent. Dissolve the residue in ethanol, take an aliquot containing < 2 mg of tocopherylquinones, and add acetate buffer soln. (pH 7) (10 ml) containing 75% ethanol. Finally, pass N through the soln., and polarograph. It was found that the tocopherols of soya-bean oil contain 13.2% of  $\alpha$ -tocopherol, 57.0% of  $\gamma$ - plus  $\beta$ -tocopherols and 29.8% of  $\delta$ -tocopherol. The corresponding percentages for cottonseed oil were 43.9, 56.1, and 0, and for sunflower-seed oil, 92.2, 0, and 7.8. The results agree well with published data.

K. R. C.

See also Abstracts—4104, Copper and Pb in org. substances. 4331, Determination of sugars. 4398, Strontium in milk. 4529, 4530, 4531, Vitamin A in mixed feeds. 4533, Pesticide residues in food.

### Sanitation

*Analysis of air, water, sewage, industrial wastes, industrial poisons.*

**4508. Field method for determining total air-borne lead.** B. E. Dixon and P. Metson (D.S.I.R., Lab. of the Gov. Chemist, Clement's Inn Passage, Strand, London). *Analyst*, 1960, **85**, 122-125.—The sample of air-borne lead is taken in the apparatus previously described (*Ibid.*, 1959, **84**, 46). The circle of test paper is disintegrated and the lead dissolved by shaking in a stoppered tube with HNO<sub>3</sub> and H<sub>2</sub>O<sub>2</sub>. An ammoniacal soln. of KCN, Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> and ammonium citrate reagent is added to the 17.5-ml mark, the tube is shaken and a soln. of dithizone in CCl<sub>4</sub> is poured through the aq. liquid until it reaches the 5-ml mark. After shaking, the layers are allowed to separate and the colour of the lower layer is compared with standard colour soln. prepared from CoCl<sub>2</sub> or CoSO<sub>4</sub> or with Lovibond glass standards. The method is precise only between  $\approx$  0.06 and 1 mg of Pb per cubic metre (the threshold toxic limit of Pb is 0.2 mg per cubic metre), but the vol. of sample may be increased or decreased.

A. O. JONES

**4509. Field method for determination of sulphur dioxide in air.** G. C. Hands and A. F. F. Bartlett (D.S.I.R., Lab. of the Gov. Chemist, Clement's Inn Passage, Strand, London). *Analyst*, 1960, **85**, 147-148.—Strips of filter-paper are impregnated with an ammoniacal soln. of zinc nitroprusside (prep. described), dried at > 40° and stored in the dark. The paper is moistened with water by means of an insufflator and fixed in the holder previously described (Dixon *et al.*, *Ibid.*, 1958, **83**, 199). Air (360 ml) is drawn through the paper and the brick-red stain produced if SO<sub>2</sub> is present is compared with a standard stain chart or with a disc of standard stains. With a 360-ml sample, concn. of 1 to 20 p.p.m. can be determined with an accuracy within  $\pm$  20%.

A. O. JONES

**4510. Determination of microgram amounts of nickel, nickel tetracarbonyl and decomposition products of the tetracarbonyl in air.** A. A. Belyakov. *Zavod. Lab.*, 1960, **26** (2), 158-159.—The air is passed at a rate of 0.5 litre per min. through a special absorption tube containing filter-paper to collect

solid particles, and then through a vessel containing 3 ml of a 1.5% soln. of chloramine B in ethanol, previously treated with 0.1 ml of HCl (1:1), to absorb nickel tetracarbonyl. The soln. is diluted with 2 ml of water, 0.2 ml of 10% NaOH soln. is added, and Ni is determined colorimetrically by means of dimethylglyoxime. The filter-papers containing the solid material are heated with 2 to 4 ml of 3% HCl soln. and Ni is determined colorimetrically.

G. S. SMITH

**4511. Determination of xylene in air in the presence of benzene and toluene.** E. Sh. Gronsberg. *Zavod. Lab.*, 1960, **26** (2), 156-158.—Selective nitration of xylene in the presence of benzene and toluene is carried out with a soln. of 10 g of  $\text{NH}_4\text{NO}_3$  in 100 ml of  $\text{H}_2\text{SO}_4$  (86%, sp.gr. 1.788). The sample of air is passed at a rate of 8 to 10 litres per hour through an absorption vessel containing 2 ml of the nitration mixture. The soln. is then heated at  $50^\circ$  for 30 min. or kept at room temp. for 1 hr. After addition of 20 ml of water, the poly-nitro compounds of xylene are extracted by shaking with 10 ml of ethyl ether for 3 min. The water layer is removed and the walls of the separating-funnel are washed down with 20 ml of water, which is then rejected. The ethereal layer is then shaken with 10 ml of water, and 5 ml of the ethereal soln. is mixed with 5 ml of ethanol and 0.5 ml of a 0.5% soln. of NaOH in ethanol, or 0.1 ml of a 5% aq. soln. of NaOH. The extinction of the soln. is measured after 5 min.

G. S. SMITH

**4512. Chemical and radiochemical analysis of radioactive atmospheric dusts.** V. Mageru, I. Gabe and D. Blănarîu (Inst. Phys., Univ., Iași). *An. Științ. Univ. "Al. I. Cuza" din Iași*, 1959, **5** (1), 119-130.—A scheme of analysis for small quantities of atmospheric dust of low radioactivity is presented, involving the addition of entrainers followed by chromatography and measurement of the activity of the separated spots. The air is filtered, the dust is washed from the filter with  $\text{H}_2\text{O}$ , and the washings are evaporated to dryness (i.r. lamp) and ignited at  $400^\circ$  to  $500^\circ$ . The weighed residue is evaporated with HF to remove  $\text{SiO}_2$  and dissolved in HCl (and  $\text{HNO}_3$  if necessary). The soln. is treated with 50  $\mu\text{g}$  each of  $\text{Ce}^{4+}$ ,  $\text{La}^{3+}$  and  $\text{Zr}^{4+}$  as "entrainers of retention" and 75  $\mu\text{g}$  each of  $\text{Sr}^{2+}$  and  $\text{Cs}^+$  as entrainers, and evaporated to 1 ml. An aliquot (0.25 ml) is chromatographed on Whatman No. 3 paper for 18 hr. at  $20^\circ$  with ethanol - butanol - acetic acid (2:1:1) (I). Two procedures are described for the identification of the isotopes. *Procedure (i)*—The part of the chromatogram carrying the rare-earth elements and Sr is cut out and eluted with 0.1N HCl. The eluate is evaporated to 0.3 ml, treated with 20  $\mu\text{g}$  each of  $\text{Sr}^{2+}$  and  $\text{Cs}^+$ , and loaded on to Whatman No. 1 paper by a modification of the method of Mierau (*Anal. Abstr.*, 1958, **5**, 311). The activity of the spot is then measured, and the chromatogram is treated with  $\text{H}_2\text{PO}_4$  dried, and developed by the ascending technique with methanol - ethanol - 2 N HCl (3:3:4) (II). After drying in air, the spots are identified by activity measurements and the successive application of Na rhodizonate (Sr) and quinalizarin (rare-earth elements). Good separations of  $^{90}\text{Zr} + ^{92}\text{Nb}$ ,  $^{144}\text{Ce}$  ( $^{144}\text{Ce}$ ) +  $^{91}\text{Y}$  and  $^{137}\text{Cs} + ^{90}\text{Sr}$  were obtained;  $^{137}\text{Cs}$  was not separated from  $^{90}\text{Sr}$ . *Procedure (ii)*—The areas of paper containing the rare-earth elements (a) and Sr (b) are cut out, eluted with HCl, and evaporated as described above. To the soln. from (a) are added 20  $\mu\text{g}$  each of  $\text{Zr}^{4+}$ ,  $\text{La}^{3+}$  and

$\text{Ce}^{4+}$ . The soln. is then loaded on to Whatman No. 1 paper, the activity of the spot is measured, and the chromatogram is treated with  $\text{H}_2\text{PO}_4$  dried, and developed with II. A good separation of  $^{90}\text{Zr} + ^{92}\text{Nb}$  from  $^{144}\text{Ce} + ^{91}\text{Y}$  is achieved. The soln. from (b) is treated as for (a) after the addition of 10  $\mu\text{g}$  each of  $\text{Ce}^{4+}$  and  $\text{Zr}^{4+}$  and 20  $\mu\text{g}$  of  $\text{Sr}^{2+}$ , and the chromatogram is developed with I;  $^{90}\text{Sr}$  is clearly separated. The activity due to  $^{90}\text{Sr}$  was found to be 0.4% of the total.

H. SHER

**4513. Determination of gases dissolved in water and vapours by gas-phase chromatography.** R. Massart and L. Missa (La Centrale des Awirs (U.C.E. Linalux)). *Bull. Cent. Belge Etud. et Docum. Eaux*, 1960, (47), 43-49.—The corrosion of structural iron by water is followed by determining the H liberated. The water containing H and other gases is equilibrated with an aliquot of inert gas (e.g., Ar) and the concn. then appearing in the gas phase is determined. A smaller aliquot of gas is withdrawn by syringe and introduced into a gas-phase chromatograph. The partition coeff. of H between gas and liquid phases is determined. Henry's law is not directly obeyed at these low concn. (1 to 100  $\mu\text{g}$  per litre).

R. M. S. HALL

**4514. Use of the glass electrode with a sodium function for the analysis of natural waters.** V. E. Goremlykin and P. A. Kryukov. *Gidrokhim. Materialy*, 1959, **28**, 180-198; *Ref. Zhur., Khim.*, 1959, (24), Abstr. No. 86,239.—A simple and convenient method for determining the concn. of  $\text{Na}^+$  with a glass electrode is described, which is applicable to natural waters of all types with a mineral content of up to 5 or 6 g of salts per litre; waters of higher mineral content may be diluted. The method cannot be used directly for acid waters, since the sodium function of the glass electrode is destroyed at low pH values; these waters must first be neutralised. The optimum equivalent ratio ( $\text{Ca}^{2+} + \text{Mg}^{2+}$ ) to  $\text{Na}^+$  in the water is  $> 6$ ; at higher ratios the sodium function of the electrodes is destroyed. The error of the "direct" determination of the concn. of  $\text{Na}^+$  is  $\pm 2\%$ ; the error of the simplified "direct" method is  $\pm 5\%$ .

C. D. KOPKIN

**4515. Determination of carbonate alkalinity in natural waters.** J. F. J. Thomas and J. J. Lynch (Dept. of Mines and Tech. Surveys, Ottawa, Ont., Canada). *J. Amer. Wat. Wks. Ass.*, 1960, **52** (2), 259-268.—The method of Larson and Henley (*Anal. Abstr.*, 1955, **2**, 3223) is shown to be applicable over a wide range of alkalinity. It eliminates the error due to the variation of the pH of the true end-point with total alkalinity. The variation of the pH of the end-point is shown graphically over a range of total alkalinity from 0 to 480 p.p.m. of  $\text{CaCO}_3$ . *Procedure*—The sample (25 to 100 ml) is titrated with standard acid at  $20^\circ$  to  $30^\circ$  to pH 4.5 (vol. required =  $x_1$  ml). The titration is then continued to pH 4.2 (vol. required =  $x_2$  ml). Then  $2x_1 - x_2$  gives the vol. of acid required to reach the true end-point of the  $\text{HCO}_3^- - \text{CO}_3^{2-}$  titration. The total alkalinity is then calculated in the usual way.

O. M. WHITTON

**4516. Suggested method for nitrate determination with 2:6-xynolen reagent.** A. M. Hartley and R. I. Asai (Univ. of Illinois, Urbana). *J. Amer. Wat. Wks. Ass.*, 1960, **52** (2), 255-258.—A spectrophotometric method is proposed. Extinction measurements are made at 322 to 324 m $\mu$ . Beer's law is obeyed over the range 0 to 125 p.p.m. of  $\text{NO}_3^-$ , and

the coeff. of variation is  $\approx 1\%$  over this range. The determination takes  $< 10$  min. Interference by  $\text{NO}_3^-$  is eliminated by the addition of solid sulphamic acid and that by  $\text{Cl}^-$  by the addition of solid  $\text{Ag}_2\text{SO}_4$  and filtration. O. M. WHITTON

**4517. Colorimetric micro-determination of copper in water: a survey of available methods.** B. Tuck and E. M. Osborn (Central Electricity Generating Board, Divisional Chem. Lab., Skelton Grange Power Sta., Leeds, England). *Analyst*, 1960, **85**, 105-110.—Five methods are investigated—(a) extraction with  $\text{CCl}_4$  of the compound formed with Na diethyldithiocarbamate; (b) measurement of the blue complex formed with bis-cyclohexanone oxalyl-dihydrazone; (c) measurement of the coloured complex formed with oxalyl-dihydrazide; (d) extraction with  $\text{CHCl}_3$  and measurement of the yellow-brown complex formed by  $\text{Cu}^+$  with neocuproin; and (e) extraction with amyl alcohol of the lilac-coloured complex formed with 2:2'-diquinolyl and its measurement. In each method the colour is measured absorptiometrically. Method (a) lacks sensitivity and selectivity; (b) and (c) are recommended if the Cu is first concentrated by ion exchange; (d) and (e) are recommended, (e) being preferred. It is unaffected by the presence of Fe, Ni, Zn, hydrazine and volatile amines.

A. O. JONES

**4518. Determination of chemically combined iodine in sea water by amperometric and catalytic methods.** R. A. Barkley and T. G. Thompson (Dept. of Oceanography, Univ. of Washington, Seattle, U.S.A.). *Anal. Chem.*, 1960, **32** (2), 154-158.—The amperometric method described is used to determine the iodine present as  $\text{IO}_3^-$ , whilst the catalytic procedure is used to determine the total iodine. The difference between the results by the two methods is used to calculate the iodine present as  $\text{I}^-$ . The amperometric method can be used for concn. of iodine down to  $5 \mu\text{g}$  per litre, with a standard deviation of  $2.1 \mu\text{g}$  per litre, and does not suffer interference from Cu and Fe at concn. up to  $300 \mu\text{g}$  per litre. The catalytic method, which is direct and rapid, can be used for concn. of iodine down to  $5 \mu\text{g}$  per litre, with a standard deviation of  $1.3 \mu\text{g}$  per litre.

K. A. PROCTOR

**4519. Study of the method of determination of oil in waters (and sewage).** J. Bouquiaux and A. Mertens (Inst. d'Hygiène et d'Epidémiologie, Belgium). *Bull. Cent. Belge Étud. et Docum. Eaux*, 1960, (110), 42-48.—Trials of the Belgian and American official methods and of a modification of the American method are reported. Full working details of the (preferred) modified method are given.

E. C. APLING

See also Abstracts—4135, Beryllium and Hg in air. 4139, Mg in natural water. 4552, Measurement of H in liquids. 4597, Detection of CO in air.

#### Agricultural analysis

Soil, fertilisers, herbicides, pesticides, animal feeding-stuffs.

**4520. Improvements in precision of high-voltage spark-excitation spectrochemical analyses of plant material by changing electrode geometry and sample treatment.** S. T. Bass and J. Connor (Dept. of Agric. Chem., Michigan Exp. Sta., Michigan State Univ., Mich., U.S.A.). *J. Ass. Off. Agric. Chem.*,

1960, **43** (1), 113-115.—For the high-voltage spark-excitation spectrochemical analysis of plant material three methods of sample preparation, viz. (i) dry-ashing and evaporating to dryness with  $\text{HCl}$ , (ii) dry-ashing and (iii) wet-ashing with  $\text{HNO}_3$ - $\text{HClO}_4$  and evaporation of excess of acids, followed in each case by the addition of  $\text{HCl}$  containing an internal standard (Co), and two types of electrode, viz. flat-polished graphite and crater electrodes, are used. The soln. is applied to the flat-polished electrode and evaporated to dryness (i.e. lamp) before excitation. A comparison of the coeff. of variation for the ratios of the intensities of several spectral lines to that of the Co line (3044 Å) shows that the flat-polished electrodes give higher precision; no ashing procedure was found to be superior, but (ii) is preferred for its rapidity.

E. J. H. BIRCH

**4521. Polarographic determination of trace elements in wheat grains. I. Determination of manganese and zinc.** S. Hasiński (Corn Technol. Lab., Inst. of Plant Cultivation and Acclimatisation, Wrocław). *Chem. Anal., Warsaw*, 1959, **4** (5-6), 837-847.—Methods of mineralisation of corn samples suitable for use in the determination of trace elements (Mn, Zn, Ni, Ti, Cu, Co, B, Mo and iodine) were examined. They consist in dry-ashing at  $> 420^\circ$  and wet-oxidation with conc.  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$  and  $\text{HClO}_4$ . The wet method was found to be more accurate. Two elements were determined, viz. Mn with  $\text{Li}_2\text{SO}_4$  soln. as supporting electrolyte, and Zn with aq.  $\text{NH}_3$ - $\text{NH}_4\text{Cl}$  soln. as supporting electrolyte. The mean error was  $\approx 10\%$ .

L. SMAROWSKI

**4522. Elimination of manganese interference in the EDTA titration of exchangeable soil magnesium.** H. H. Cheng and L. T. Kurtz (Agronomy Dept., Univ. of Illinois, Urbana, U.S.A.). *J. Agric. Food Chem.*, 1960, **8** (1), 24-26.—The interference of Mn with EDTA titrations of Ca and Mg is eliminated by pptn. with ferrocyanide. Procedure—Samples of soil (20 g) are soaked in 100 ml of neutral N ammonium acetate for 1 hr. and 10-ml aliquots of the filtered extract are titrated for Ca and Mg by diluting suitably, buffering to pH 10 and adding 10 drops each of 2% aq. KCN soln. to remove heavy metals, triethanolamine to remove Al, 4% aq.  $\text{K}_4\text{Fe}(\text{CN})_6$  soln. to precipitate Mn, and Eriochrome black T soln. as indicator. Titration is then effected with EDTA (disodium salt) from a micro-burette in the usual way. Magnesium alone is titrated similarly after pptn. of Ca with 20% aq. sodium tungstate soln. The titration can be made directly in the presence of the  $\text{Mn}_4\text{Fe}(\text{CN})_6$  if there is  $< 1$  milli-equiv. of Mn per 100 g of soil, but filtering is needed for larger amounts. The method is tested with soln. of known concn.

E. J. H. BIRCH

**4523. The use of lanthanum chloride to prevent interferences in the flame-photometric determination of exchangeable calcium in soils.** C. H. Williams (Div. of Plant Industry, C.S.I.R.O., Canberra, Australia). *Anal. Chim. Acta*, 1960, **22** (2), 163-171.—Interference by  $\text{Al}$ ,  $\text{PO}_4^{3-}$ ,  $\text{SO}_4^{2-}$  or  $\text{SiO}_4^{4-}$  has been prevented by the addition of La to the solution.

E. G. CUMMINS

**4524. A rapid method for the determination of organic carbon in soil.** L. J. Mebius (Inst. for Soil Fertility, Groningen, Netherlands). *Anal. Chim. Acta*, 1960, **22** (2), 120-124.—The method of Tiurin-Simakov (*Pochvuovedenie*, 1931, 36, and 1957, 72)

has been modified to give results for which the coeff. of variation of a single determination is 1-2% and which agree with those obtained by the standard, dry-combustion, method. The dry-combustion method has been found to be the only reliable one for saline soils and those containing inorganic oxidisable substances. E. G. CUMMINS

**4525. New method for the determination of sesquioxides and titanium dioxide in the total chemical analysis of soils and the separation of aluminium from iron.** N. N. Safronkova. *Izv. Mold. Fil. Akad. Nauk SSSR*, 1959, [4(49)], 41-50; *Ref. Zhur., Khim.*, 1959, (24), Abstr. No. 86,238.—The conditions under which the reaction of salts of Al, Fe and Ti with K Na tartrate liberates the equivalent amount of acid are found. This is the basis of the titrimetric method for the determination of total  $Al_2O_3 + Fe_2O_3 + TiO_2$  in soils, which comprises alkali titration of a mixture of the test soln., K Na tartrate, and  $CaCl_2$  in the presence of phenolphthalein. The method is fairly rapid, and total  $Al_2O_3 + Fe_2O_3 + TiO_2$  can be determined in the presence of silicic and phosphoric acids. With certain modifications, the method for separating Al from Fe, based on the pptn. of Al with ammonium benzoate in weak acetic acid medium, is used;  $Fe^{3+}$  are reduced to  $Fe^{2+}$  with sodium dithionite. C. D. KOPKIN

**4526. Study of alpha-radioactivity in the soil and in biological material by spectrum determination.** R. D. Lonati and F. Tonolini (Lab. CISE, Milano, Italy). *Energia Nucleare*, 1960, 7 (2), 107-110 (in English).—The low  $\alpha$ -activity in some samples of soil, plant-ash, grass and bones (of sheep grazed on the grass) has been measured by an improvement of the procedure described previously (Lonati *et al.*, *Nuovo Cimento*, Ser. X, 1958, 7, 133). The finely ground prepared sample ( $\approx 20$  mg) is mixed with 10% aq.  $Na_2SiO_3$  soln. ( $\approx 10$  mg) and spread on the electrode in the ionisation chamber (emitting surface 110 sq. cm; very low background). After  $\approx 40$  hr. the spectrum (2 to 9 MeV) is recorded, and the measurement of the same sample is repeated after approx. one month. The lower limit of measurable total  $\alpha$ -activity is from 1 to  $5 \times 10^{-12}$  C per g, according to the background count. Plant-ash ( $\approx 10$  g) should be prepared for spectroscopy by heating at  $200^\circ$  with  $H_2SO_4$  and HF until the silicate is eliminated, treating the residue with hot and then cold  $H_2O$ , centrifuging and, finally, drying the residue ( $\approx 3$  g) at  $80^\circ$ . The results are reported and discussed in relation to the distribution of  $^{226}Ra$ ,  $^{230}Th$ ,  $^{208}Pb$ ,  $^{238}U$ ,  $^{210}Po$  and other activities in the sample. W. J. BAKER

**4527. Rapid method for the examination of feed mixtures containing added copper and zinc.** W. T. Binnerts (Lab. Fysiol. d. Dieren, Landbouwhogeschool, Wageningen, Netherlands). *Chem. Weekbl.*, 1960, 56 (6), 81.—Feed mixtures containing 0.1% of  $CuSO_4$  yield a blue coloration after the addition of a few drops of zincon soln. (1 pellet of NaOH and 130 mg of zincon per 100 ml) and stirring for a short time. Feed mixtures containing very small amounts of Cu remain red. To test for 50 p.p.m. of Zn, a small amount of the sample is mixed with buffer soln. (pH 9) and zincon soln. (1 drop) is added. The dark colour produced can readily be distinguished from the orange-red colour given by samples containing smaller amounts of Zn. M. J. MAURICE

**4528. Determination of sugar in silages and forages.** H. G. Wiseman, J. C. Mallack and W. C. Jacobson (Dairy Cattle Res. Branch, ARS, Agric. Res. Center, Beltsville, Md., U.S.A.). *J. Agric. Food Chem.*, 1960, 8 (1), 78-80.—A copper reduction method is modified so that clarification is carried out on the alcoholic extract before de-alcoholisation, thus avoiding formation of gummy residues. *Procedure*—Chopped samples of silage or forage (20 g) are extracted in a Waring Blendor for 10 min. with 80% ethanol, and the extract is filtered through a bed of Darco G-60 and Celite 535 (1:3) sandwiched between layers of Celite 535. The bed is washed with 300 ml of 80% ethanol and the total extract is made up to 750 ml. A 30-ml aliquot is stirred magnetically for 15 min. with Dowex 50 (0.5 g) and Dulolite A-4 (1.75 g) (washed free from reducing substances) or Dowex 50W-X8 (0.4 g) and Dowex 3 (1.4 g). The de-ionised soln. is filtered on glass wool and the resins are rinsed with 80% ethanol and 25 ml of hot water. The filtrate is evaporated to 1 to 2 ml to remove ethanol, and inverted by standing overnight with N HCl (25 ml). After inversion the soln. is brought to pH 7 with NaOH soln. and made up to 50 ml. Aliquots (5 ml for fresh material or 10 ml for silage) in 25-mm test-tubes fitted with magnetic stirrers are treated with Somogyi sugar reagent (with  $KIO_3$ ,  $Na_2HPO_4$  and NaOH) (*J. Biol. Chem.*, 1945, 160, 61) (5 or 10 ml) and heated to boiling for 15 min. After cooling the soln., 1 or 2 ml of 2.5% KI soln. is added to form an upper layer, followed by 3 ml of 1.5 N  $H_2SO_4$  or 5 ml of 1.8 N  $H_2SO_4$ , and the pptd.  $Cu_2O$  is oxidised by the liberated iodine by stirring for 1 min. Excess of iodine is titrated with 0.005 N  $Na_2S_2O_3$  to a starch end-point. The alkaline buffering of the reagent ensures that glucose and fructose reduce Cu to the same extent. E. J. H. BIRCH

**4529. Study of the method for vitamin A in mixed feeds.** D. B. Parrish (Kansas Agric. Exp. Station, Manhattan, Kan., U.S.A.). *J. Ass. Off. Agric. Chem.*, 1960, 43 (1), 30-34.—The results of vitamin-A determinations by a standard method (*Ibid.*, 1958, 41, 57; 1959, 42, 61) by 14 laboratories on two samples of mixed feed are reported. No significant differences were observed from the use of Woelm alumina containing 4%, 5% or 6% of  $H_2O$  for chromatography. No significant differences between carotene results were obtained when samples of 20 g, 40 g and 80 g were used. Coeff. of variation for the vitamin-A content were 27% for a 40-g sample containing 670  $\mu$ g per lb and 10% for a sample containing 1185  $\mu$ g per lb. Recommendations for the amendment of the standard method are made. E. J. H. BIRCH

**4530. Statistical procedure for estimating vitamin-A assay variation caused by particulate distribution of dry vitamin A in feed samples.** R. W. Lehman (Res. Lab., Distillation Products Industries Div., Eastman Kodak Co., Rochester, N.Y., U.S.A.). *J. Ass. Off. Agric. Chem.*, 1960, 43 (1), 15-20.—If the particles of dry vitamin-A supplements are uniform in size and vitamin content, and are randomly distributed throughout the feed, the standard deviation of the assay would be  $\sqrt{n}$ , where  $n$  is the number of particles expected in a given sample. Size analyses of various commercial additives show that the particles are not uniform, so that statistically weighted average particles must be defined. It is shown that for an approximately S-shaped curve of the cumulative percentage of particles passing a mesh *vs.* the mesh size, the



particle diameter corresponding to the mesh through which 60% of the particles pass is a suitable figure. The results lead to rather large assay variations in the normal 40-g sample. For precise analysis larger samples and higher fortification levels are suggested.

E. J. H. BIRCH

**4531. Use of large samples in the determination of vitamin A in mixed feeds fortified with dry vitamin-A supplements.** F. H. Tinkler, J. B. Hanley and R. W. Lehman (Distillation Products Ind., Div. of Eastman Kodak Co., Rochester, N.Y., U.S.A.). *J. Ass. Off. Agric. Chem.*, 1960, **43** (1), 25-34.—The particulate nature of vitamin-A dry supplements leads to large sampling errors in a 40-g sample of feed (Lehman, *Anal. Abstr.*, 1960, **7**, 4530). The AOAC procedure is modified for a 400-g instead of a 40-g sample; the assay sample should be obtained by sampling at least 25 lb of the feed. The main modification consists of the extraction of an aliquot part of the saponification liquor after the insol. matter has settled. Results for a number of supplemented feeds are given; the mean coeff. of variation (122 determinations) was 2.45%.

E. J. H. BIRCH

**4532. Paper chromatography of 3-amino-1:2:4-triazole.** L. C. Mitchell (Div. of Food, Food and Drug Admin., Dept. of Health, Education and Welfare, Washington, D.C., U.S.A.). *J. Ass. Off. Agric. Chem.*, 1960, **43** (1), 87-88.—Various methods of paper chromatography of 3-amino-1:2:4-triazole (I) (technical and analytical grades) were studied; the best procedure is as follows. Spots (10 µg) of I dissolved in dimethylformamide are applied to Whatman No. 1 paper and chromatographed by the ascending technique for  $\approx 3$  hr. with dioxan-water (4:1). The spots are best revealed by spraying with ethanolic ammoniacal AgNO<sub>3</sub> soln. and heating to 130° for 10 to 15 min.

E. J. H. BIRCH

**4533. Identification of pesticide residues in extracts of fruit, vegetables and animal fats. II. Rapid qualitative chemical tests for captan and methoxychlor.** W. P. McKinley and S. I. Graham (Food and Drug Lab., Canada Dept. of Nat. Health and Welfare, Ottawa). *J. Ass. Off. Agric. Chem.*, 1960, **43** (1), 89-91.—Captan is detected at the Canadian tolerance level (15 to 20 p.p.m.) by extracting 900 to 1100 g of material with 335 ml of benzene for 30 min. in a roller stripper. The extract is dried with anhyd. Na<sub>2</sub>SO<sub>4</sub> and an aliquot (50 ml) is evaporated and the residue is dissolved in 10 ml of CHCl<sub>3</sub> and added to a column of Florisil, followed by the washings of the flask with benzene containing 3% of CHCl<sub>3</sub>. The column is eluted with benzene containing 3% of CHCl<sub>3</sub> and 150 ml of the eluate is collected. Duplicate portions of the eluate (200 µl) are concentrated and placed on Whatman No. 1 paper which has been washed and dipped in a 14% soln. of 2-phenoxyethanol in ethyl ether. One spot is sprayed with AgNO<sub>3</sub> soln. to detect all pesticides, and the other with a soln. of 0.5% of ZnCl<sub>2</sub> and 0.5% of diphenylamine in acetone. The development of an intense green spot within 60 sec. of exposure to u.v. light confirms the presence of captan. Extracts are prepared similarly for methoxychlor, but it is unnecessary to re-dissolve in CHCl<sub>3</sub>. After chromatography on Florisil, 100 µl of the eluate is analysed by the method of McKinley and Mahon (*Ibid.*, 1959, **42**, 725), and the presence of methoxychlor is confirmed by evaporating 1 ml of eluate, adding 0.1 ml of fuming HNO<sub>3</sub> to the residue and, 30 sec. later,

2 ml of 1:83 to 1:87 N Na methoxide in methanol, with shaking. A deep-blue colour confirms the presence of methoxychlor. Possible interferences from plant pigments and other pesticides are discussed.

E. J. H. BIRCH

**4534. Assay of Co-Ral [O-3-chloro-4-methyl-2-oxo-2H-1-benzopyran-7-yl OO-diethyl phosphorothioate] in technical materials and formulated products.** P. F. Kane, C. J. Cohen, W. R. Betker and D. MacDougall (Chemagro Corp., Kansas City, Mo., U.S.A.). *J. Agric. Food Chem.*, 1960, **8** (1), 26-29.—Hydrolysis of Co-Ral (I) in N aq. and N isopropyl alcoholic KOH and back-titration with 0.5 N HCl gives 2 different series of inflections on the pH curves, the only one common to both being that at pH 7.5, corresponding to the formation of 3 moles of acid per mole of I. These acids are probably the phosphorothioic acid, HCl and a carboxylic acid liberated by the opening of the lactone ring. The hydrolysis with isopropyl alcohol gives the better end-point in the back-titrations, and the method is suitable for determining pure I. The u.v. spectra of I and of chloromethylumbelliferone (II) (the most likely interfering compound), in methanol (10 µg and 5 µg per ml, respectively) are measured. I has a double peak with max. at 290 and at 315 mµ, and II a peak at 330 mµ. In 50% methanol containing Na<sub>2</sub>CO<sub>3</sub>, II has a max. at 380 mµ, where I is practically non-absorbing. *Procedure*—I (0.2 g in 100 ml of dioxan and 5 ml of 0.1 N HCl) is diluted to 250 ml with methanol and the extinction is measured at 290 mµ. To correct for the presence of II, to 50 ml of the undiluted I soln. is added 50 ml of 1% aq. Na<sub>2</sub>CO<sub>3</sub> soln. and the extinction at 380 mµ is read within 15 min. The amount of II calculated from a calibration curve, and multiplied by 0.67, is subtracted from the value of I from the first absorption determination.

E. J. H. BIRCH

**4535. Determination of Dyrene and cyanuric chloride in technical materials.** P. F. Kane and K. G. Gillespie (Chemagro Corp., Kansas City, Mo., U.S.A.). *J. Agric. Food Chem.*, 1960, **8** (1), 29-32.—The hydrolysis of Dyrene (2:4-dichloro-6-o-chloroanilino-sym.-triazine) in neutral or acid soln. with liberation of Cl<sup>-</sup> is shown to be much slower than that of cyanuric chloride (its usual contaminant) and neither is hydrolysed appreciably during the time it takes to titrate Cl<sup>-</sup> at 0°. This forms the basis for assays of Dyrene. *Procedure for total hydrolysable Cl*—A 0.5-g sample is heated under reflux for 30 min. with 50 ml of N NaOH. The condenser is rinsed down, the soln. is neutralised with dil. HNO<sub>3</sub>, and a 10-ml excess is added. The contents are titrated potentiometrically with 0.1 N AgNO<sub>3</sub> with a bright silver and a glass electrode. *For water-hydrolysable Cl*—A 5-g sample is hydrolysed by heating under reflux with water for 10 min. The Cl<sup>-</sup> are titrated as before. *For ionisable Cl*—To a 5-g sample is added 100 ml of ice-cold water containing enough chipped ice to maintain the temp. during titration. After stirring for 10 min. to dissolve the chloride, the soln. is titrated as before. The times in the two last procedures are critical if partial hydrolysis of the Dyrene or of both non-ionisable chlorine compounds is not to take place.

E. J. H. BIRCH

**4536. Colorimetric determination of residues of phorate and its insecticidally active metabolites.** P. A. Giang and M. S. Schechter (Entomol. Res. Div., U.S. Dept. of Agric., Beltsville, Md., U.S.A.). *J. Agric. Food Chem.*, 1960, **8** (1), 51-54.—Phorate

[OO-diethyl]S-(ethylthio)methylphosphorodithioate] and its toxic oxidation products give a red - violet colour with chromotropic acid due to the production of formaldehyde. Recoveries are better if the material is first oxidised to sulphone with perbenzoic acid. *Procedure*—The plant sample (100 g) is macerated with  $\text{CHCl}_3$ , strained, filtered through anhyd.  $\text{Na}_2\text{SO}_4$  and evaporated to 100 ml. A dil. soln. (5 ml) of perbenzoic acid in benzene (concn. not critical) is added and after 10 min. the soln. is passed through a Nuchar - Hyflo Super-cel column; the percolate and  $\text{CHCl}_3$  washings are washed with 100 ml of 0.5%  $\text{Na}_2\text{S}_2\text{O}_5$  soln. and three 150-ml portions of satd. NaCl soln., and filtered through anhyd.  $\text{Na}_2\text{SO}_4$ . The solvent is evaporated by distilling through a three-bulb Snyder column, and the last traces of solvent are removed at room temp. under vacuum. The waxy residue is washed by swirling with water on the steam bath, and the material is cooled and filtered through a 0.5 to 1.0-cm layer of Attaclay - Hyflo Super-cel to remove the waxes. The combined filtrate is extracted with  $\text{CHCl}_3$ , which is dried and evaporated as before. The residue is dissolved in 3 ml of 0.5 N NaOH and heated for 1 min. on a hot-water bath. Chromotropic acid reagent (1.6% of the sodium salt in  $\text{H}_2\text{SO}_4$ ) (3 ml) is added and after heating the mixture for 45 min. on a boiling-water bath, then cooling and making up to 6 ml, the extinction is measured at 570 m $\mu$ . Beer's law is obeyed up to 100  $\mu\text{g}$  and recovery is  $\approx 90\%$ . Calibration curves are prepared from pure soln. of phorate in  $\text{CHCl}_3$ .

E. J. H. BIRCH

**4537. Determination of Trithion crop residues by cholinesterase-inhibition measurement.** G. G. Patchett and G. H. Batchelder (Stauffer Res. Lab., Richmond, Calif., U.S.A.). *J. Agric. Food Chem.*, 1960, **8** (1), 54-57.—Trithion [S-(p-chlorophenylthio)methyl OO-diethyl phosphorodithioate] is converted into strong cholinesterase inhibitors by oxidation of the S in the phenylthio group, and this is used for the determination of residues. *Procedure*—A 200-ml extract is prepared by tumbling a 100-g sample of the crop material with benzene for 1 hr. Portions (5 ml) of the benzene extract are treated with acetic acid-30%  $\text{H}_2\text{O}_2$  soln. (5:1) (3 ml) and heated at 75° for 20  $\pm$  0.5 min. After cooling the tubes, 5 ml of water is added and, after shaking the tubes, aliquots of the benzene layer (containing 0.02 to 0.15  $\mu\text{g}$  of Trithion) are placed in 20-ml beakers. Liquid paraffin (4 drops) is added to soften waxes. After evaporation of benzene and any acetic acid, 9.0 ml of water is added and the beaker is heated for 10 min. on a hot-plate at 110° to 130°. After cooling this oxidised Trithion (and even leaving overnight), 1.0 ml of pooled human plasma, chosen and mixed so that the pH after addition to the test material is 1.8 to 2.0, is added and the mixture is incubated at 37.5° for 70 min. A 1.0-ml aliquot is treated with 1 ml of buffer soln. (2.67 g of barbitone, 0.545 g of  $\text{KH}_2\text{PO}_4$ , 44.7 g of KCl and 12 ml of N NaOH, adjusted with HCl so that the pH in making up to 500 ml is 7.9 to 8.0) and the pH is measured. The buffered soln. are incubated at 37.5° for 120 min., then cooled, and the pH is measured again. The percentage cholinesterase inhibition is measured as  $100[1 - (\text{sample } \Delta \text{pH} / \text{blank } \Delta \text{pH})]$ , where  $\Delta \text{pH}$  is the change in pH as a result of the incubation. Standard curves are prepared with pure Trithion. A methyl cyanide extraction procedure is described for samples containing much oil or wax. Many other pesticides whose oxidation products have

cholinesterase-inhibiting properties would probably interfere. The stability of Trithion, the efficiency of the procedure and the recovery are discussed. The max. precision is  $\pm 0.005 \mu\text{g}$ .

E. J. H. BIRCH

**4538. Micro-determination of endrin.** E. J. Skerrett and E. A. Baker (Res. Sta., Long Ashton, Bristol, England). *Analyst*, 1960, **85**, 148.—The use of a boron trifluoride reagent in the determination of small amounts of dieldrin has been described (*Ibid.*, 1959, **84**, 376). The method is applicable to the determination of endrin, but the optimum time of heating was found to be 30 min. and the optimum temp. 40°. The sensitivity of the method is only about one-half that of the method for dieldrin.

A. O. JONES

**4539. Pre-chromatographic purification of insecticides from insect-tissue extracts.** J. J. Menn, M. E. Eldefrawi and H. T. Gordon (Dept. of Entomol. and Parasitol., Univ. of Calif., Berkeley, U.S.A.). *J. Agric. Food Chem.*, 1960, **8** (1), 41-42.—Paper chromatograms of insecticides and their metabolites extracted from insect tissues are often spoiled by the presence of lipid matter. A preliminary treatment is described to separate the required material. *Procedure*—Insects are homogenised in 5 ml of acetone, the soln. is dried with a pinch of anhyd.  $\text{Na}_2\text{SO}_4$ , and centrifuged. The residue is re-extracted twice and the combined extract is evaporated under N to 30 to 50  $\mu\text{l}$ , and is transferred by a capillary tube to the middle of a piece of Whatman No. 4 paper (2.5 in.  $\times$  1 in.) cut to a point. A 0.5% soln. of NN-dimethyl-p-1-naphthylazoaniline (1  $\mu\text{l}$ ) is applied to the same place as a visual indicator of the complete removal of DDT, demeton or phorate [OO-diethyl S-(ethylthio)methyl phosphorodithioate] from the spot. The spot is then treated by an upward or downward washing procedure with methyl cyanide, which removes the required substances from the spot but substantially leaves the lipid material. In each case the methyl cyanide soln. of the material is collected from the point cut in the paper, and is used to start the definitive chromatogram. Examples of the use of the method are given. E. J. H. BIRCH

See also Abstracts—**4341**. Chromatography of derivatives of ethylenebisdithiocarbamic acid. **4342**. Determination of organophosphorus comp. **4400**. Zn and Cu in soil extracts and stable manure. **4500**. Thiamine in corn-meal enrichment mixture.

## 5.—GENERAL TECHNIQUE AND APPARATUS

### General

**4540. Use of zirconium crucibles for sodium peroxide fusions.** R. P. Anibal (Strategic-Udy Processes, Inc., Niagara Falls, N.Y.). *Anal. Chem.*, 1960, **32** (2), 293.—Crucibles of zirconium are better than those of iron or nickel for determinations of Cr in chrome ore. Low results, due to a peroxy zirconium compound reducing some Cr, can be avoided by re-oxidising the Cr. Alternatively, filtration before acidification will give acceptable results (0.1 to 0.2% low). A second fusion in a zirconium crucible is necessary in determinations of P.

R. M. S. HALL

4541. An electromicro-balance for weighing fibres. F. R. Morgan (British Leather Manuf. Res. Ass., Egham, Surrey). *J. Sci. Instrum.*, 1960, **37** (2), 53-54.—The balance pan is attached to the pointer of a moving-coil milliammeter. The null position of the pointer is observed by a microscope and is restored by passing current through the milliammeter. The balance has a capacity of 1.5 mg and weighs to about 1  $\mu$ g. (Cf. Hales and Kynaston, *Analyst*, 1954, **79**, 702.) G. SKIRROW

4542. A convenient weighing-tube for volatile liquids in carbon-hydrogen and Dumas nitrogen micro-determination. Tetsuo Mitsui and Chieko Furuki (Dept. of Agric. Chem., Coll. of Agric., Kyoto Univ., Japan). *Mikrochim. Acta*, 1960, (2), 169-174 (in English).—The weighing-tube described and illustrated is a capillary (0.5 mm inside and 3.5 mm outside diam.; length 70 mm) of transparent quartz, in which a platinum wire (0.07 mm in diam. and 80 mm in length), doubled and with 10 mm of the bent end folded back, is inserted into the middle. When a liquid is introduced into the capillary it is retained in the middle of the tube by the bent wire, and diffusion of the vapour from the capillary is minimised. Results show that this sampling tube can be used satisfactorily for the micro-determination of carbon, hydrogen and nitrogen. B. B. BAUMINGER

4543. Density bottles. British Standards Institution (2 Park Street, London, W.1). B.S. 733: 1952. Amendment No. 2 (23.5.60).

4544. Graduated measuring cylinders. British Standards Institution (2 Park Street, London, W.1). B.S. 604: 1952. Amendment No. 4 (11.5.60).

4545. Apparatus for routine analysis. III. Automatic measures. G. Lindley (English Electric Co., Ltd., Bradford). *Lab. Practice*, 1960, **9** (2), 111-112.—Soln. in routine use are raised by suction from stock bottles below the bench into calibrated measuring vessels. The error of delivery is  $\pm 1\%$ , and both accuracy and reproducibility exceed those attained when graduated cylinders are used. The measures are available commercially.

J. H. WATON

4546. Tables for use in the calibration of volumetric glassware. British Standards Institution (2 Park Street, London, W.1). B.S. 1797: 1952. Amendment No. 2 (30.5.60).

4547. Magnetically agitated Van Slyke gas-analysis apparatus. Anon. *Lab. Practice*, 1960, **9** (2), 93-94.—The agitation of the reactants in this commercially available apparatus is highly efficient, and results as precise as those obtained with a mechanically shaken model are given. Advantages of the new model are the rigid junction between pipette and manifold, the elimination of the risk of mercury or other chemicals being thrown out during agitation, the possibility of emptying or loading during agitation, the elimination of fracture of glass-ware during use and stripping, and the ease of dismantling. J. H. WATON

4548. Improvements in or relating to apparatus for measuring the concentration of a component of a gaseous mixture. Central Electricity Generating Board, W. G. Cummings and M. W. Redfeam. Brit. Pat. 837,477; date appl. 12.2.57.—The gaseous

mixture is passed upwards through a countercurrent absorption column through which a reagent liquid is passed downwards. The column comprises an upright tube surrounding an inner member which has a helical element wound tightly around it, or formed integrally with it, providing a helical path in the annular space down which the reagent liquid may run. The external cross-sectional area of the helix is less than that of the outer tube, to leave a path for the flow of the gaseous mixture in the axial direction outside the helix. J. M. JACOBS

4549. Method and apparatus for the continuous determination of reactive constituents of gas mixtures. Ruhrchemie A.-G. Brit. Pat. 834,816, date appl. 8.6.56. Germany, date appl. 11.6.55.—An apparatus for the continuous determination of traces of a constituent in a gas mixture by means of a change in colour of a liquid reagent (e.g., 0.05 to 0.15%, by vol., of oxygen in industrial gases with aq. ammoniacal CuCl) comprises a mixing nozzle, proportioning pumps for passing the gas mixture and the reagent at pre-determined rates into the nozzle, a comparator cell through which the reagent is passed to the mixing nozzle, a reaction path of sufficient length to permit complete reaction between the reagent and the constituent being determined, a gas trap for separating the unabsorbed gas from the reagent, a test cell through which the reagent is passed after separation of the unreacted gas, means for regenerating the reagent disposed between the test cell and the proportioning pump, a light source for illuminating the comparator and test cells, and photometric means for indicating and recording the difference in colour between the liquids in the two cells. J. M. JACOBS

4550. Improvements in or relating to the continuous determination of the quantity of liquid-soluble gas in a gas mixture. K. T. Källe. Brit. Pat. 833,926, date appl. 22.11.57. Sweden, date appl. 5.12.56.—Gas-absorption apparatus for the continuous determination of the quantity, in a gas mixture, of a gas which is difficultly sol. in the liquid employed for its absorption, e.g., CO<sub>2</sub> in water, comprises a vessel having an inlet and an outlet for continuous passage of absorption liquid, a first pump for introducing the gas mixture into the vessel below the liquid level therein, and a second pump arranged to extract gas not absorbed by the liquid from the top of the vessel through a conduit connected to means for indicating the gas pressure in the conduit. The liquid is supplied to the vessel at a constant pressure, the liquid outlet from the vessel is restricted to maintain the pressure in the vessel, and the outlet from the vessel to the conduit is restricted to prevent escape of liquid (cf. Brit. Pat. 714,898). J. M. JACOBS

4551. Simplification of Haldane's apparatus for measuring carbon dioxide concentration in respired gases in clinical practice. E. J. M. Campbell (Med. Unit, Middlesex Hosp., London). *Brit. Med. J.*, 1960, 457-458.—The apparatus described differs from the standard Haldane apparatus in having no absorption pipette or compensating burette; it has a three-way tap on the calibrated burette and a syringe in place of the mercury levelling bulb. Reproducibility is within  $\pm 0.05\%$ , and agreement with the standard method is within  $\pm 0.1\%$ .

H. F. W. KIRKPATRICK

**4552. Improvements in or relating to devices for measuring the hydrogen content of liquids.** Westinghouse Electric Corp. Brit. Pat. 838,169; date appl. 31.1.58. U.S.A., date appl. 7.2.57.—A device for continuously monitoring the dissolved-hydrogen concn. of a liquid system, e.g., a pressurised water system, comprises an elongated tube of hydrogen-permeable material (palladium) suspended in a vessel which communicates freely with the liquid system, so as to be filled with the liquid from the system. The tube is hermetically sealed relative to the interior of the vessel, and is coupled to a manometer calibrated to read directly the dissolved-hydrogen concn. of the water or other liquid.

J. M. JACOBS

**4553. Simple siphon device for fraction collection.** E. Haahti (Univ. Hospital, Turku, Finland). *Scand. J. Clin. Lab. Invest.*, 1959, **11** (3), 304.—The apparatus described is suitable for use with solvents of low sp. gr. which will not operate drop counters having contact points. The solvent acts on a liquid manometer containing dil. salt soln., which is the conducting medium between 2 contact wires, these being connected to an amplifier and relay, or to a pulse counter. A volume error of < 10% is obtainable.

D. B. PALMER

**4554. Simple separating apparatus for solvent extractions with solvents lighter than water.** T. W. Steele (Gov. Metallurg. Lab., Univ. Witwatersrand, Johannesburg, S. Africa). *Analyst*, 1960, **85**, 153-154.—A thin-walled polyethylene bottle is fitted with a stopper carrying a vertical glass tube with a stopcock, the exit end of the tube being curved slightly outwards. The bottle containing the solvent and the aq. liquid is shaken with the stopcock closed. When the layers have separated the bottle is placed in a laboratory clamp, the stopcock is opened and the bottle is squeezed by means of the clamp until the aq. layer reaches the top of the bore of the stopcock. A fresh portion of the solvent is then introduced through the stopcock by releasing the clamp. Since the polyethylene bottle can be collapsed to only half its vol., the relation between the size of the bottle and the relative vol. of aq. and solvent layers must be suitably arranged.

A. O. JONES

**4555. Apparatus for routine analysis. II. Fractionating pipette.** G. Lindley (Works Chem. Lab., English Electric Co. Ltd., Bradford). *Lab. Practice*, 1960, **9** (1), 40.—The construction and use are described of pipettes provided with double-bore stopcocks facilitating rapid washing and filling by means of pump suction. These pipettes show saving of time in routine operations and improved safety in the measuring of toxic liquids.

E. C. AFLING

#### Chromatography, ion exchange, electrophoresis

**4556. An equilibration device for paper chromatography.** R. S. Potter, E. M. Lindsay and R. Chayen (Dept. of Chem. Engng, Univ. Coll. London). *J. Chromatography*, 1960, **3** (2), 202-203 (in English).—A simple, air-tight device is described for suspending papers above the solvent in a tank and for lowering them when equilibration is achieved. Diagrams are given.

P. D. PARR-RICHARD

**4557. Slit-feeding apparatus for paper chromatography with some examples concerning phosphatides.** H. G. Bungenberg de Jong, J. T. Googeven (Dept. Med. Chem., Univ. of Leyden, Holland). *Proc. Kon. Ned. Akad. Wet.*, B, 1960, **63** (1), 1-14 (in English).—The factors to be considered in the construction of a device for reproducible chromatographic separations are discussed. For phosphatide separations it is shown that the position of the immersion line on the chromatogram is more important than the starting position of the material in characterising chromatographic displacement, that  $R_F$  values depend largely on the height of the solvent front, that separation is better in vessels having a large air volume, and that the conditions within the apparatus should be exactly reproducible for each separation. To fulfil these requirements, two types of apparatus were designed and are fully described, one for strips the other for large sheets of paper. Basically, the device consists of a horizontal tube, containing the mobile phase, having a slit into which the paper fits, so that it dips into the mobile phase. The reservoir can be filled from outside the chromatographic tank once the paper is in position. Only small volumes of the mobile phase are required,  $\approx 3$  or 7 ml, respectively, thus allowing fresh solvent to be used for each new separation. The apparatus is easily cleaned, and details of the method of use, and precautions necessary to obtain good results, are given. An example of the use of the apparatus for the separation of phosphatide mixtures is shown. For this separation S. & S. paper 2043b impregnated with  $\text{SiCl}_4$  is used, with a mobile phase consisting of diisobutyl ketone-acetic acid-water (10:5:1). The chromatograms are run at 20° in the dark, and the individual compounds are revealed by staining with acid fuchsine-uranil nitrate soln. and viewing under u.v. light. The best resolution is attained when large sheets of paper are used instead of strips.

D. B. PALMER

**4558. Chromatographic gas analysis sample control system.** Foxboro Co. Brit. Pat. 833,864; date appl. 24.6.58. U.S.A., date appl. 11.7.57.—The system repeatedly produces gas samples of fixed vol. and constant mass to a high degree of accuracy by cancelling out barometric pressure effects and by varying the pressure of a constant-vol. gas sample in response to temp. effects on a body of reference gas. A fixed-vol. conduit is provided in conjunction with a pair of opposed bellows. One bellows is filled with the reference gas and the other is pneumatically connected with the fixed-vol. conduit as an operating bellows. The operating bellows has a vent valve, operated by the back pressure of a nozzle, which in turn is variably restricted by a baffle which moves according to the differential pressure between the bellows. Thus with suitable switch arrangements with respect to the fixed-vol. conduit, the pressure and therefore the density of the sample gas in the fixed-vol. conduit is varied according to the temp. changes in the reference bellows, with the result that the mass of the gas in the fixed-vol. conduit is maintained constant.

J. M. JACOBS

**4559. Gas-liquid partition chromatography: column behaviour and its reproduction criteria for favourable column behaviour.** Buddhaddev Sen (Coates Chem. Lab., Louisiana State Univ., Baton Rouge, U.S.A.). *Anal. Chim. Acta*, 1960, **22** (2), 130-142.—Recommendations are made for deter-



mining the optimum column conditions and the reproducibility of column behaviour.

E. G. CUMMINS

**4560. Formation of volatile compounds on gas-liquid chromatography columns.** M. E. Kieser and D. J. Sissons (Long Ashton Res. Sta., Bristol, England). *Nature*, 1960, **185**, 529.—The findings of Weurman and Dhont (*Anal. Abstr.*, 1960, **7**, 3557) on the formation of volatile esters on chromatographic columns with polyoxyethylene glycol 400 as stationary phase were confirmed. The stock polyoxyethylene glycol was found to contain formic acid and formaldehyde. Pretreatment of the polyoxyethylene glycol as suggested by Adlard (Symposium on vapour-phase chromatography, Inst. Petroleum, London, 1960) by heating at 100°, at 0.01 torr, for 16 hr. has yielded satisfactory chromatograms of alcohols.

S. BAAR

**4561. Factors affecting the use of gas-liquid chromatography for the separation of large samples. Sample-inlet system, distribution coefficient of solute, and amount of liquid in stationary phase.** W. J. de Wet and V. Pretorius (Dept. of Agric. and Phys. Chem., Univ. Pretoria, S. Africa). *Anal. Chem.*, 1960, **32** (2), 169–174.—In gas chromatography the column efficiency decreases as the sample vol. increases, and the highest efficiencies can be obtained for large samples by introducing the sample in the form of a concentrated plug, by choosing a stationary phase in which the distribution coeff. of the solute is small, and by using relatively large amounts of stationary phase.

K. A. PROCTOR

**4562. Studies on vapour-phase chromatography. III. The effect of support and of stationary liquid on the relative retention value.** Tomio Fukuda (Fac. of Engng, Yokohama Univ., Minami-ku, Yokohama). *Japan Analyst*, 1959, **8** (10), 627–630.—The relative retention volumes (toluene = 1.00) of non-polar compounds at 100° are almost independent of the nature of the support (Celite 545 and Isolite) and the content (10 to 33% by wt.) of the stationary phase (liquid or solid paraffin and polyoxyethylene glycol), whereas those of polar compounds are largely affected. With Celite containing > 20% of liquid paraffin or > 10% of polyoxyethylene glycol, the difference is small.

**IV. Relative retention values of some organic compounds.** Tomio Fukuda and Toshizi Omori. *Ibid.*, 1958, **8** (10), 630–633.—Data are given for the retention volumes of 60 low-boiling org. compounds on three columns of Celite 545 containing 33% by wt. of liquid paraffin, polyoxyethylene glycol and dinonyl phthalate, respectively, at 100°. Results are compared with those of other workers.

K. SAITO

**4563. Construction of long lengths of coiled glass capillary.** D. H. Desty, J. N. Haresnape and B. H. F. Whyman (Res. Centre, The British Petroleum Co. Ltd., Sunbury-on-Thames, Mddx.). *Anal. Chem.*, 1960, **32** (2), 302–304.—A versatile laboratory machine is described for drawing out glass capillary with a wide range of diameter and wall thickness in lengths of several hundred feet coiled into a compact helix.

K. A. PROCTOR

**4564. Analytical accuracy in gas chromatography using thermal-conductivity detectors.** A. Weinstein (Dept. of Fuel Technol., Pennsylvania State Univ., Pa., U.S.A.). *Anal. Chem.*, 1960, **32**

(2), 288–290.—Changes in pressure and flow rate consequent on sample introduction have been investigated with a molecular sieve column and argon as the carrier gas, and the results indicate that an adsorption phenomenon, rather than viscosity differences, is responsible for these effects. The results suggest also that the method of calibration with pure substances leads to systematic errors because of the mutual effect that the components of a mixture have on each other's peak parameters. Such errors decrease as the sample size diminishes, and are independent of base-line stability.

K. A. PROCTOR

**4565. Apparatus for detecting the presence of organic gases and vapours.** Imperial Chemical Industries of Australia and New Zealand, Ltd. Brit. Pat. 838,189; date appl. 2.7.58. Australia, date appl. 4.7.57.—The electrical conductivity of a hydrogen flame, or the flame of a mixture of hydrogen and an inert gas, e.g., nitrogen, burning in oxygen or diluted oxygen, e.g., air, is increased to a marked degree when an organic gas or vapour is given access to the flame. A mixture of nitrogen and hydrogen ( $\approx 7:3$ , by vol.) is burnt at the tip of a stainless-steel jet made from a hypodermic needle, which acts as one electrode, at such a flow rate that a flame of  $\approx 1$  to 2 cm in height is produced. A second electrode of fine steel gauze is placed  $\approx 1$  cm above the flame. The electrodes are connected to a battery and a resistor and the variation in the voltage drop across the resistor brought about when an organic gas or vapour is fed into the combustion zone of the burner is measured, e.g., by means of a vibrating-reed electrometer.

J. M. JACOBS

**4566. Registration of gas-chromatography fractions by means of a mercury-drop potentiometer.** J. Surový (Chem. Fac., Inst. Chem. Technol., Bratislava, Czechoslovakia). *Chem. Listy*, 1960, **54** (3), 263–268.—The simple apparatus described is suitable for the automatic registration of gaseous fractions at const. pressure and can be used in conjunction with the usual laboratory apparatus for recording current and voltage.

J. ŽYKA

**4567. High-temperature seal for gas-chromatography detectors.** R. L. Faley and J. F. Long (Polychemicals Dept., E. I. du Pont de Nemours & Co., Victoria, Tex., U.S.A.). *Anal. Chem.*, 1960, **32** (2), 302.—The use of a Crawford Swagelok tube fitting to mount thermal-conductivity detectors allows easy insertion and removal and ensures freedom from leaks or abnormal electrical noise, for ambient temp. up to 500° and pressures up to 50 p.s.i.g.

K. A. PROCTOR

**4568. Simple non-gassing electrodes for use in electrophoresis.** R. Neihof and S. Schuldiner (U.S. Naval Res. Lab., Washington, D.C., U.S.A.). *Nature*, 1960, **185**, 526–527.—Conditions suitable for the use of palladium-hydrogen electrodes are described which allow them to be used to provide a high current density for electrophoresis without the evolution of gas. An "alloy" PdH<sub>x</sub> is formed at the cathode and, if its formation is rapid compared with the combination of atomic H with the palladium surface, no H will be evolved till the ratio of H to Pd is 0.9. No gases will be evolved at the anode while the electrode has a store of atomic H. The anode must be cathodically charged with hydrogen before use. Palladium is more suitable than

platinum for high current densities because of its greater absorptive capacity for H. Three electrodes are described in detail. The simplest form is palladium inserted into the electrolyte used. This electrode must be pre-charged with the calculated amount of H. The second electrode described serves as a bi-electrode; it separates the solution leading to the electrophoresis cell and the solution surrounding the primary electrode. In this form equivalent amounts of H are released and taken up by the opposite faces of the bi-electrode. In the third form, the palladium tube anode is constantly flushed with hydrogen gas and the cathode is open to the air. At the cathode, atomic H derived from the reduction of hydronium ions migrates through the walls of the tube and reacts with atmospheric oxygen to yield  $H_2O$ . Hydrogen dissolved in the anode migrates through the walls and reacts at the solution interface. This form of electrode allows current to be passed in one direction for an indefinite time without gas formation at either electrode.

S. BAAR

**4569. Electrophoresis of amino acids on cellulose powder.** C. Montant and J. M. Touze-Soulet (Lab. de Cryptogamie, Fac. des Sciences, Toulouse). *Bull. Soc. Chim. Biol.*, 1960, **42** (1), 161-166.—A simple electrophoresis apparatus is described and detailed instructions are given for the separation of 40-mg quantities of amino acids on a cellulose powder support with a buffer soln. (pH 3.9) of acetic acid-pyridine-water (10:3:487). Precautions are taken to minimise evaporation, and electrophoresis is carried out in a cold room for 14 hr. at 250 V and 80 mA.

E. C. BUTTERWORTH

**4570. Rapid paper ionophoresis using organic buffers in water-formamide and water-urea.** L. N. Werum, H. T. Gordon and W. Thornburg (Dept. of Entomol. and Parasitol., Univ. of California, U.S.A.). *J. Chromatography*, 1960, **3** (2), 125-145 (in English).—A series of buffers from pH 3.3 to 9.3, in 30% formamide, is used to obtain electropherograms in  $> 3$  hr.; urea replaces formamide for the separation of proteins. Evaporation and adsorption from these systems is low. Mobilities are measured with respect to a set of reference dyes; knowledge of the relative mobilities at pH 3.3 and 9.3 often permits classification of an unknown compound. Ninhydrin or alloxan is used for identification of amines and amino acids, periodic acid-benzidine for carbohydrates, serine and threonine, and bromophenol blue for denatured proteins.

P. D. PARR-RICHARD

### Optical

**4571. Recording apparatus for traces of oxygen.** J. Pierrain. *Chim. Anal.*, 1960, **42** (2), 78-82.—Between 30 and 150 p.p.m. of O in nitrogen is determined by its oxidation of an ammoniacal soln. of  $CuCl$  to  $Cu^{II}$ , which is then measured photometrically. There is no interference from H, ethylene, acetylene or CO. The system is made entirely automatic, and the reduction of  $Cu^{II}$  to  $Cu^I$  by copper turnings in the storage vessel enables the  $CuCl$  to be re-cycled. Such an apparatus has run for more than 3 years.

J. H. WATON

**4572. Photometer for continuous determination of uranium in radioactive process streams.** F. A. Scott and R. D. Dierks (Hanford Laboratories

Operation, General Electric Co., Richland, Wash., U.S.A.). *Anal. Chem.*, 1960, **32** (2), 268-272.—A modified, single-beam filter photometer is described for the continuous colorimetric monitoring of uranyl nitrate in process streams. The instrument is very stable (short-term variation  $< 1\%$ ) and has a simple and rugged, remotely located sensing unit.

K. A. PROCTOR

**4573. Determination of several elements by the use of the Zeiss-Jena flame photometer.** V. Patrovský (Ústav Nerostných Surovin, Prague). *Chem. Listy*, 1960, **54** (3), 268-273.—The use of this instrument is described. This type of apparatus isolates spectral bands, mainly by means of interference-type colour filters.

P. G.

**4574. Organic solvents in flame spectrometry.** A. Püschel and S. Eckhard (Max-Planck-Inst. f. Eisenforschung, Düsseldorf). *Arch. Eisenhüttenw.*, 1959, **30** (12), 731-735.—A review is given of recent work on the use of organic solvents in flame spectrometry. Alcohols and other organic solvents give a higher flame intensity than water. This effect is discussed in relation to surface tension, viscosity and degree of dispersion of the solution in the flame. The effects on the intensity of direct and indirect dispersion, flame temperature and chemical reactions in the flame are considered. These effects are illustrated by experiments on salts dissolved in propanol, ethanol, methanol and mixtures of ethanol and water. The flame intensity obtained increases in the series propanol to methanol.

M. G. SEAMAN

**4575. An especially simple method for spectrochemical spot analysis.** R. Geyer, K. Doerffel and H. Kirst (Tech. Hochschule f. Chem., Halle, Saale, Germany). *Z. anal. Chem.*, 1960, **172** (5), 326-333 (in German).—Samples coated with a transparent insulating varnish are suitable for spot spectroanalysis: the coating adheres to the sample but can be penetrated at will. Creep of the spark is minimised. The sample area may be as little as 0.05 sq. mm. The resin or varnish must be free from metallic impurities. The method is well suited to the examination of welded seams and particularly of the homogeneity of the seam and of the distribution of Mn (0.1 to 1.0%) within the seam. Results with these very small sample areas are evaluated statistically.

J. P. STERN

**4576. Gas analyser for automatic measurement of low concentrations of nitrogen in argon by a spectrophotometric method.** V. V. Aleksandrov and M. T. Borok (Design Bureau of Analytical Apparatus Construction, Acad. Sci., USSR). *Zavod. Lab.*, 1960, **26** (2), 214-217.—The gas at a pressure of 0.3 torr is excited in a discharge tube by means of a high-frequency electrodeless discharge. Part of the radiation passes through a PS-11 colour filter (max. of transmission  $\approx 350 m\mu$ ) and part through a SZS-11 colour filter (max. of transmission  $\approx 450 m\mu$ ) and then on to separate photo-elements. The photo-currents are related to the concn. of N and Ar, respectively. The gas must first be passed through a drying chamber. An automatic apparatus for use with a flowing gas mixture is described.

G. S. SMITH

**4577. Standard addition technique in flame spectrometry.** T. E. Beukelman and S. S. Lord, jun. (Jackson Lab., E. I. du Pont de Nemours and

Co., Wilmington, Delaware, U.S.A.). *Appl. Spectroscopy*, 1960, **14** (1), 12-17.—The addition of known quantities of a metal to a solution already containing a small unknown amount of that metal may be used as a means of estimating the original content by logarithmic extrapolation of the working curve. The method is useful for samples with undefined matrices or for the determination of traces without extensive calibration. Examples are given for the determination of Ca in the presence of phosphate, and of Ca and Na in a polyoxyethylene glycol. The mathematical treatment of the data shows that three additions which are the same as, twice and four times the residual amount are optimum. Under these conditions the relative error caused by extrapolation is approx. seven times the relative error in the original intensity measurements.

P. T. BEALE

**4578. The Schumann region and its analytical possibilities.** G. Milazzo (Ist. Sup. Sanit., Lab. Chim., Roma, Italy). *R.C. Ist. Sup. Sanit.*, 1960, **23** (2), 133-139.—The practical difficulties encountered in emission spectroscopy in the spectral region below 2000 Å (the Schumann region) and new techniques for minimising these difficulties are discussed. It is concluded that the use of this spectral region is becoming practicable for analytical purposes, particularly for those elements (e.g., S, P and C) which do not have suitable lines at higher wavelengths.

E. C. APLING

**4579. [Quantitative] spectroscopic analysis.** Hilger & Watts, Ltd. [Inventor: W. B. Diamand]. Brit. Pat. 833,570; date appl. 21.3.57.—A crucible containing a sample of the substance to be analysed is heated (by subjecting the crucible to electron bombardment) to a temp. sufficient to vaporise the sample completely, and the vapour is excited to emit the characteristic spectrum of the sample (by heating to a sufficient high temp., by a glow discharge, or by electron bombardment) whilst applying a control to the heating of the crucible (feedback from a pyrometer which measures the temp. of the sample) to keep the vapour temp. constant. The relative intensities of the characteristic spectral lines emitted are measured.

J. M. JACOBS

**4580. Calculating board for spectrochemical analysis.** D. R. Stoss (Materials and Processes Lab., Large Steam Turbine-Generator Dept., General Electric Co., Schenectady, N.Y., U.S.A.). *Appl. Spectroscopy*, 1960, **14** (1), 24.—The board consists of a plotting table, a long vertical cursor, inscribed with a Seidel density function and a two-cycle log scale, and two horizontal sliding scales. One of these carries one of a family of interchangeable calibration scales, corresponding to photographic emulsions with different contrasts or at different wavelengths, the other is a two-cycle log scale. Working curves are drawn on the plotting surface. Background corrections can be applied if required.

P. T. BEALE

**4581. An electrical spectrographic calculator.** S. Epstein (Fed. Metals Div., American Smelting and Refining Co., L.A., Calif., U.S.A.). *Appl. Spectroscopy*, 1960, **14** (1), 7-11.—Spectral line transmission values are applied to the calibrated potentiometers, and the electrical circuit, which is based on analogue computer principles, solves the equation of the working curve of the element being determined, providing this is a straight line. If it is

non-linear, the intensity ratios are calculated by the instrument, and percentages are read off from the plotted working curve. The effect of background and of variations of contrast factor with wavelength may be easily compensated for in the instrument.

P. T. BEALE

**4482. Absorption spectrophotometry of samples of low transparency.** J. Braunbeck (Bodenseewerk Perkin-Elmer & Co., G.m.b.H., Überlingen, Bodensee). *Angew. Chem.*, 1960, **72** (1), 31-33.—By inserting an attenuating filter in the compensating beam of a double-beam recording spectrophotometer (e.g., Perkin Elmer Model 21) the indicated transmission of a semi-opaque sample may be enhanced. This technique enables i.r. and presumably other spectra to be determined directly on samples of paper, woven synthetic fibres and plastic films.

T. R. ANDREW

**4583. Continuous reference beam attenuator for infra-red spectrophotometry.** J. P. Luongo (Bell Telephone Lab. Inc., Murray Hill, N.J., U.S.A.). *Appl. Spectroscopy*, 1960, **14** (1), 24-25.—The attenuator consists of a frame carrying 5 thin brass vertical vanes  $\frac{5}{16}$  in. wide and spaced  $\frac{5}{16}$  in. apart. When the frame is normal to the reference beam there is approx. 96% transmission, and when it is rotated to make an angle of  $> 45^\circ$  with the beam there is no transmission. Intermediate positions give a continuously variable attenuation between 0 and 96% transmission, which can be reproduced to within 1% by means of a simple pointer and scale. The fitting described is for a Perkin Elmer Model 21 spectrophotometer.

P. T. BEALE

**4584. Preparation of micro Nujol mulls for infra-red analysis.** L. J. Lohr and R. J. Kaier (Explosives Dept., E. I. du Pont de Nemours & Co., Gibbstown, N.J., U.S.A.). *Anal. Chem.*, 1960, **32** (2), 301.—A stainless-steel micro-capsule is described for the preparation of mulls from only 3 to 5 mg of sample. The mulls are prepared by the standard procedure, and the resolution obtained by the micro-technique is said to be equal to or better than that obtained by the usual technique.

K. A. PROCTOR

**4585. Versatile die for preparation of potassium bromide windows.** H. T. Grendon and H. L. Lovell (College of Mineral Industries, Pennsylvania State Univ., Pa., U.S.A.). *Anal. Chem.*, 1960, **32** (2), 300-301.—The die described has a number of useful features and is easily constructed from inexpensive materials. The windows are formed very rapidly and are consistently clear, retaining their clarity for several weeks when properly stored. The size and shape of the windows can easily be varied.

K. A. PROCTOR

**4586. Simple technique for polishing barium fluoride windows.** D. S. Erley, B. H. Blake and A. W. Long (Spectroscopy Lab., The Dow Chemical Co., Midland, Mich., U.S.A.). *Appl. Spectroscopy*, 1960, **14** (1), 25-26.—Conc. HCl is used as a slurring agent in conjunction with an appropriate polishing powder ("Shamva" for repolishing or "No. 600 Aloxit" for rough blanks) and a pitch lap.

P. T. BEALE

**4587. Apparatus for continuous fluorescence X-ray spectrographic analysis of solutions.** W. J. Campbell (Eastern Exp. Sta., Bur. of Mines, College Park, Md., U.S.A.). *Appl. Spectroscopy*,

1960, **14** (1), 26-27.—The construction of a cell, suitable for continuous monitoring of a pumped-through solution, is described. The speed of response to variations in the concn. of  $Zn^{2+}$  is given as an example. P. T. BEALE

4588. Precision null-point atomic absorption spectrochemical analysis. H. V. Malmstadt and W. E. Chambers (Dept. of Chem. and Chemical Engng. Univ. of Illinois, Urbana, U.S.A.). *Anal. Chem.*, 1960, **32** (2), 225-232.—By combining a null-point technique with atomic absorption, increased precision, accuracy, selectivity and sensitivity can be obtained with a low-cost instrument. At the same time the need for linear working characteristics or working curves is eliminated. Sodium and K have been determined in the 1 to 100-p.p.m. range with coeff. of variation of < 0.5%.

K. A. PROCTOR

See also Abstracts—4226, Spectrophotometric analysis of binary mixtures. 4349, C-H stretching frequencies.

### Thermal

4589. Micro-determination of mixtures of substances with the aid of the critical miscibility temperature. F. Gölls (Inst. Pharmakog., Univ. Graz, Austria). *Mikrochim. Acta*, 1960, (2), 299-315 (in German).—Soln. of ethanol in water containing up to 40% of ethanol can be analysed on the micro scale by adding vinyl cyanide in known amounts and observing the min. temp. at which complete miscibility occurs. Mixtures of acetic acid and water containing up to 7% of acetic acid can be analysed similarly by adding *n*-butanol. Values are given of the critical miscibility temp. for various proportions of the three liquids in both systems. H. M.

4590. Apparatus to measure high-temperature melting-points by the capillary-tube method. L. A. Rechaizer and A. D. Tevebaugh (Gen. Elec. Res. Lab., Schenectady, N.Y.). *Rev. Sci. Instrum.*, 1960, **31** (2), 215-216.—The apparatus is designed to measure melting-points up to 600° and consists of a nickel cylinder supported on a ceramic thermocouple tube and heated by a Nichrome wire coil. The capillary tube containing the sample fits in the nickel cylinder and rests on the thermocouple hot junction. The whole apparatus is housed in a glass tube open at the upper end to permit insertion of the capillary. Melting of the sample is observed through a small hole in the nickel cylinder or by observing the temp. at which a thin weighted glass rod resting on the sample falls through to the bottom of the tube. G. SKIRROW

### Electrical

4591. Apparatus for determining electro-conductivity and composition of solutions. V. I. Ermakov. *Zavod. Lab.*, 1960, **26** (2), 229-230.—The apparatus was constructed for the purpose of measuring automatically the change in conductivity of a solution that was diluted continuously with solvent at a known rate. Into the soln. of known initial concn., placed in an induction coil of a high-

frequency generator, solvent enters under a constant head of pressure and the total vol. is kept constant by means of a tube at the surface connected to a suction pump. From the known rate of flow of solvent the concn. at any given time can be calculated. A curve showing the relation between conductivity and the log of the concn. is automatically recorded. G. S. SMITH

4592. Potentiostat for electro-gravimetric analysis. J. F. Herringshaw and P. F. Halfhide (Chem. Dept., Imperial Coll. of Sci. and Technol., London). *Analyst*, 1960, **85**, 69-74.—In the instrument described, the e.m.f. of the cell formed by the working and reference electrodes is connected in series-opposition with a potentiometer set to the required e.m.f. The resulting "error" voltage is amplified, and the amplified signal operates a motor that by means of a transformer alters the current applied to the electrolytic cell. Improvements in design have eliminated the need for high stabilisation of the high-tension supply, and provide good smoothing and discrimination in the electrolysis current. A. O. JONES

4593. Potentiostat for electrochemical analysis. Yu. A. Klyachko, Yu. D. Labut'ev and V. A. Mil'chev. *Zavod. Lab.*, 1960, **26** (2), 217-219.—A potentiostat for phase analysis by anodic dissolution of samples of surface area up to 8 sq. cm is described. The potential can be held constant to  $\pm 2$  mV over the range  $-2$  to  $+2$  V vs. the S.C.E.

G. S. SMITH

4594. New apparatus for electrolytic isolation of carbides and non-metallic inclusions from steel. A. Fiala, J. Macek and V. Stádler (Z.V.I.L., Plzeň, Czechoslovakia). *Hutn. Listy*, 1960, **15** (1), 55-56.—The described apparatus differs from the Klinger-Koch system in (i) increased dissolving capacity of samples, (ii) the possibility of adjusting to the same current density for each sample, (iii) continuous dissolution of the anode from all sides, (iv) less consumption of electrolyte. The apparatus is similar to that of Garside *et al.* (*Anal. Abstr.*, 1958, **5**, 1521) and enables various electrolytes to be used; the electrolyte can be cooled during the procedure which can be carried out in an inert atmosphere. The glass in some parts of the apparatus was advantageously replaced by polystyrene. J. ZÝKA

4595. Theory and application of the rotating-disc electrode. W. Vielstich (Inst. f. phys. Chem. Univ., Bonn, Germany). *Z. anal. Chem.*, 1960, **173** (1), 84-87 (in German).—The current-diffusion relationship is developed for a rotating-disc electrode and its application to the study of kinetics of reactions is outlined. T. R. ANDREW

4596. Improvements in and relating to fluid analysis, [more particularly the continuous measurements of one constituent in a stream of process gas]. Union Carbide & Carbon Corp. [Assignee of S. B. Spracklen, D. N. Campbell and C. G. Fellows]. Brit. Pat. 832,703; date appl. 12.2.57. U.S.A., date appl. 13.2.56.—A stream of suitable reagent is brought continuously into contact with a flowing stream of sample gas mixture containing the constituent to be measured, which is present in a concn. of the order of p.p.m. and operates to effect a change in the ionic content of the reagent solution. The stream of treated reagent solution is then brought into contact



with one of a pair of parallel spaced electrodes, while another stream of untreated reagent solution is concurrently brought into contact with the other electrode so as to maintain a liquid interface between the streams of solution and provide a "dynamic concn. cell" whereby a potential is developed across the electrodes which is proportional to the change in ionic content of the stream of treated reagent solution. This potential is then measured as an indication of the concn. of the constituent to be measured in the sample of the gas mixture.

J. M. JACOBS

**4597. Improvements in and relating to apparatus for detecting carbon monoxide.** Coal Industry (Patents) Ltd. [Inventor: R. Valentine]. Brit. Pat. 835,933; date appl. 11.4.57 (Addition to Brit. Pat. 756,662, dated 29.10.53).—The apparatus described in the parent patent is modified by using transistors in place of thermionic valves in the electric circuit which produces the signal, as the instruments are intended mainly for use in mine workings where an explosive atmosphere may be present.

J. M. JACOBS

**4598. Polarographic apparatus with triangular sweep and variable speeds with synchronised pen recorder.** P. Papoff, L. Grifone and G. Zuliani (Modena Univ., Italy). *Ric. Sci.*, 1960, **30** (1), 159-161.—An apparatus is described capable of applying the potential at variable speed between 3 to 300 mV per sec. and giving the potential graph directly. The oxidation and reduction diagrams are obtained in the same cycle and the apparatus is particularly suitable for studying the reversibility of an electrochemical process.

L. A. O'NEILL

**4599. Polarographic determination of very small amounts by means of the stationary mercury electrode.** E. N. Vinogradova and G. V. Prokhorova (M. V. Lomonosov Moscow State Univ.). *Zavod. Lab.*, 1960, **26** (1), 41-45.—A mercury drop is placed in a cup formed at the upturned end of a capillary tube fitted with a platinum contact, or else a drop of known size is caused to form at the end of an upturned capillary tube by opening a tap connecting a graduated tube containing mercury with the capillary. The metal to be determined is deposited on the surface of the drop at a suitable potential and an anodic polarogram is subsequently taken. Since deposition and dissolution of the metal occur at the surface of the drop, whilst diffusion within the drop is occurring all the time, it is necessary to control carefully the conditions, including the duration of cathodic polarisation. Because the anodic stage never results in complete removal of the metal from the drop, a fresh drop must be used each time. The method is applied to the determination of  $10^{-4}$  % of Pb in Zn acetate and potassium alum.

G. S. SMITH

**4600. Potentiometric titrations.** H. L. Kies (Anal. Chem. Lab., Tech. Univ., Delft, The Netherlands). *Chem. Weekbl.*, 1960, **56** (2), 13-20.—The following subjects are discussed—(a) potentiometry at zero current, (b) potentiometry at constant current, and (c) potentiometry at changing current. Recent modifications of classical potentiometry are reviewed. It is shown that potentiometry with a small constant current is often preferable to the classical technique, especially when two indicator electrodes are used. After a discussion of "polarovolttry," potentiometry without an external voltage

source is mentioned and the advantages and disadvantages of potentiometry and amperometry are compared. (60 references.)

M. J. MAURICE

**4601. The theory and practice of polarography in melts.** G. J. Hills and J. E. Oxley (Imperial College, London, S.W.7). *Z. anal. Chem.*, 1960, **173** (1), 5-10 (in English).—Gas-flushed and stationary solid electrodes have been used with a cathode-ray polarograph to study the behaviour of LiCl-KCl melts. It is shown that such melts are not indifferent because of the solubility of alkali metal liberated by pre-electrolysis.

T. R. ANDREW

**4602. Glass parts of polarographic apparatus.** S. G. Mafranovskii and F. S. Titov (N. D. Zelinsky Inst. of Org. Chem., Acad. of Sci., USSR, Moscow). *Zhur. Anal. Khim.*, 1960, **15** (1), 121-123.—Designs for a polarographic cell, a dropping-mercury electrode, supplied with a beak for reducing drop time, non-polarisable electrodes and a vessel for the saturation of nitrogen with solvent vapours are described.

A. BURWOOD-SMITH

**4603. Polarography in anhydrous ethylenediamine.** G. Schöber and V. Gutmann (Inst. f. Anorg. u. Allg. Chem. Tech. Hochschule, Wien). *Z. anal. Chem.*, 1960, **173** (1), 2-4 (in German).—The behaviour of 24 reducible ions in liquid  $\text{NH}_3$  and in ethylenediamine is reported. Sodium nitrate, LiCl and tetraethylammonium nitrate have been used as basal electrolytes. Good polarographic curves are obtained for  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{Li}^+$ .

T. R. ANDREW

**4604. Experiences with the cathode-ray polarograph.** M. Herrmann (Farbwerke Hoechst A.-G., Frankfurt/Main). *Z. anal. Chem.*, 1960, **173** (1), 21-23 (in German).—A review of the performance of the cathode-ray polarograph in an industrial laboratory is given. The sensitivity of the instrument is estimated to be about 100 times higher than that of a conventional polarograph.

T. R. ANDREW

**4605. Alternating-current and square-wave polarography.** H. Schmidt (Inst. f. phys. Chem., Univ., Bonn, Germany). *Z. anal. Chem.*, 1960, **173** (1), 73-79 (in German).—A review of the underlying principles is given.

T. R. ANDREW

**4606. Alternating-current polarographic analysis by harmonic measurements.** H. H. Bauer (Section of Agric. Chem., Univ. of Sydney, Australia). *J. Electroanal. Chem.*, 1960, **1** (3), 256-258 (in English).—Electrodes at which redox processes are occurring behave as non-linear electrical elements, but the capacitive impedance of the electrical double layer behaves as an almost perfectly linear electrical element. It follows that measurements of higher harmonics, rather than of the fundamental frequency, can give information about redox processes without interference from the double layer. A comparatively large alternating voltage (10 to 30 mV) should be used. The second harmonic peaks are sharper and the base current is relatively smaller than with normal a.c. polarography, so that the selectivity and sensitivity are greatly superior.

A. R. ROGERS

**4607. Pulse polarography.** G. C. Barker and A. W. Gardner (A.E.R.E., Harwell, Berks., England). *Z. anal. Chem.*, 1960, **173** (1), 79-83 (in English).—The performance of the square-wave polarograph (cf. Barker and Jenkins, *Analyst*, 1952, **77**, 685) has been improved by discarding the square-wave voltage in favour of polarising pulses of short duration. For presentation of derivative polarograms, the pulses are of 50 mV amplitude, superimposed on a slowly changing polarising voltage, while for normal polarograms the amplitude may vary from 0 to 1 V and is proportional to the elapsed time from the start of the sweep. The limiting sensitivity for the new instrument is  $10^{-8}$  M for reversibly reduced ions and  $5 \times 10^{-8}$  M for irreversibly reduced ions, compared with  $4 \times 10^{-8}$  M and  $10^{-6}$  M for the original square-wave instrument. T. R. ANDREW

**4608. "Tastpolarographie."** A. W. Elbel (Atlas-Werken A.-G., Bremen, Germany). *Z. anal. Chem.*, 1960, **173** (1), 70-73.—Several advantages are claimed for the technique of Strehlow *et al.* (*Polarograph. Ber.*, 1957, **5**, 62) in which the change in current over only a small portion of the life of a drop is recorded. These advantages include improved resolution, reduction in condenser current and less dependence of the response on potential. T. R. ANDREW

**4609. Electrochemical device for chemical analysis.** Beckman Instruments, Inc. [Inventor: L. C. Clark, jun.]. Brit. Pat. 838,980; date appl. 8.8.57.—In a cell for use in quant. polarographic analysis, the anode and cathode pair are electrically connected through a "captive" electrolyte, which is protected from turbulence and is separated and electrically insulated from the solution to be analysed by a barrier permeable to the constituent the concn. of which it is desired to measure, but impermeable to all the other constituents of the solution that might have an effect on the electrical characteristics of the cell, e.g., a polyethylene membrane when the cell is to be used for determining the oxygen content of a gas or a solution. J. M. JACOBS

**4610. Potentiometric and amperometric titrations with EDTA. Mercury and copper as indicator electrodes.** G. Guérin, J. Desbarres and B. Trémillon (Lab. de Chim. Anal., École de Physique et de Chimie, Paris, France). *J. Electroanal. Chem.*, 1960, **1** (3), 226-240 (in French).—Electrochemical phenomena at mercury and copper electrodes in various media and in the presence of EDTA and its complexes with metal cations were studied by plotting the current-potential curves. The electrochemical reactions are fairly rapid in acid, but slow in ammoniacal medium. The various possibilities of titrating  $\text{Cu}^{2+}$  with copper electrodes and  $\text{Hg}^{2+}$  with mercury electrodes as well as other cations such as  $\text{Zn}^{2+}$  were examined. A. R. ROGERS

**4611. Automatic recording velocity-servo potentiometric titrator.** M. T. Kelley, D. J. Fisher and E. B. Wagner (Oak Ridge Nat. Lab., Tenn., U.S.A.). *Anal. Chem.*, 1960, **32** (1), 61-66.—The apparatus described utilises a servo-mechanism to control the rate of addition of titrant. The titrator is designed for general potentiometric methods and is

applicable to both radioactive and non-radioactive samples on a micro or macro scale.

K. A. PROCTOR

**4612. Use of electrodes screened by some polymers in the potentiometric indication of the end-point.** K. Komers (Dept. Anal. Chem., Inst. Chem. Technol., Pardubice, Czechoslovakia). *Sb. Věd. Prac., Vysoké Školy Chem.-Technol., Pardubice*, 1959, 113-119.—*Preparation of the electrodes*—Prepare 0.5 to 5% soln. of polystyrene or poly(methyl methacrylate) in acetone, of poly(vinyl chloride) in cyclohexanone and chloroprene in  $\text{CHCl}_3$ , immerse the cleaned electrodes in the soln. and dry in air for 20 min. Good results with these electrodes were obtained in various redox and argentimetric titrations. J. ZÝKA

**4613. High-frequency titrimeter and its use.** E. Pungor (Dept. of Inorg. and Anal. Chem., L. Eötvös Univ., Budapest, Hungary). *Chem. Zvesti*, 1959, **13** (12), 823-826.—The apparatus operates at a frequency of  $\approx 130$  Mc/s. Examples are given of its use in neutralisation titration and in studying the stability of soln. in sealed glass ampoules. J. ZÝKA

**4614. Use of an unbalanced bridge circuit in high-frequency titrimetry.** J. M. Walker, J. L. Lambert and L. D. Ellsworth (Dept. of Chem. and Physics, Kansas State Univ., Manhattan, U.S.A.). *Anal. Chem.*, 1960, **32** (1), 9-13.—The use of a modulated off-balance radio-frequency signal originating from the detector side of a high-frequency bridge has been studied as a method of carrying out high-frequency titrations. Data are obtained as volt-meter readings and are easily plotted against vol. without calculations. A new titration cell incorporating magnetic stirring is described. K. A. PROCTOR

**4615. Limits of concentration measurement of a high-frequency titrimeter with a frequency of about 130 MHz.** E. Pungor and L. Balázs (Inst. Inorg. and Anal. Chem., L. Eötvös Univ., Budapest, Hungary). *Mikrochim. Acta*, 1960, (1), 118-126 (in German).—Titration curves were obtained for acid-base and precipitation reactions by using the high-frequency titrimeter described by Pungor and Huber (*Z. anal. Chem.*, 1957, **154**, 1). The lower limits of detection were  $\text{HCl}$  1  $\mu\text{g}$  per ml, acetic acid 20  $\mu\text{g}$  per ml,  $\text{Cl}^-$  2  $\mu\text{g}$  per ml and  $\text{SO}_4^{2-}$  10  $\mu\text{g}$  per ml. In the titration of  $\text{SO}_4^{2-}$ , Ba acetate soln. is used as titrant, and ethanol and solid  $\text{BaSO}_4$  are added to the sample soln. to aid the pptn. of  $\text{BaSO}_4$ . W. T. CARTER

**4616. Coulometric titrations.** E. Barendrecht (Cent. Lab. Staatsmijnen in Limburg, Geleen, Netherlands). *Chem. Weekbl.*, 1960, **56** (4), 37-48.—General applications of coulometry at constant potential and at constant current are reviewed. Further points of discussion are—the material and current yield of electrode processes, apparatus for the control of the potential of the working electrode and of the electrolysis current, and methods for end-point indication and for the measurement of applied amounts of electricity. Examples of coulometric titrations are given. The discussed technique is especially useful in the determination of trace elements. (66 references.) M. J. MAURICE

**4617. Electronic methods in chemistry. II. High-frequency titrations with a crystal-controlled oscillator.** J. Pokorný (Dept. Inorg. Chem., Inst. Chem. Technol., Prague). *Chem. Listy*, 1959, **53** (11), 1141-1144.—A simple arrangement was constructed with the use of a high-frequency oscillator controlled by a piezoelectric quartz crystal which stabilises the frequency of the oscillator with an accuracy up to  $10^{-8}$  c/s. The titration vessel is switched into the anodic circuit as a part of the capacity and the changes of amplitude of the oscillations are measured to give the changes of anodic current or of the potential. Good results were obtained in titrating 0.1N HCl, HNO<sub>3</sub>, HClO<sub>4</sub>, H<sub>2</sub>SO<sub>4</sub>, H<sub>3</sub>PO<sub>4</sub> and oxalic acid with NaOH soln. Two neutralisation steps were observed in titrating H<sub>2</sub>SO<sub>4</sub>, H<sub>3</sub>PO<sub>4</sub> and oxalic acid.

J. ZÝKA

**4618. Studies on automatic continuous coulometric titration. I. Principle and construction of a titrator and its use for acid-base titration.** Akira Takahashi (Denkishiki Kagakuken Kenkyujo, Kichijoji, Musashino, Tokyo). *Japan Analyst*, 1959, **8** (10), 661-666.—An apparatus is described and illustrated in which the current generated with glass and calomel electrodes is amplified and applied, by means of an automatic electronic zero balancing system, to the control of the d.c. (obtained by rectification from an a.c. source) used to generate NaOH by electrolysis of NaCl soln., so that the mixture of sample soln. and electrolyte is maintained at the end-point of the reaction. The sample soln. and electrolyte are fed to the titration cell by means of pumps driven by a synchronous motor. Results are quoted for the titration of H<sub>2</sub>SO<sub>4</sub> soln.; Na<sub>2</sub>SO<sub>4</sub> did not interfere. The compensation of errors due to variations in the temp. of the electrolysis and titration cells, and in the frequency of the a.c. source, is discussed.

K. SAITO

**4619. Amperometric titrations.** W. M. Smit (Anal. Chem. Lab., Rijksuniv., Utrecht, Netherlands). *Chem. Weekbl.*, 1960, **56** (3), 25-29.—Amperometric titrations can be carried out with one or with two indicator electrodes. The relationships between current and concentration are derived for reversible and irreversible redox systems. Means for increasing the precision are given. Two applications are mentioned, viz, the titration of U<sup>4+</sup> with KMnO<sub>4</sub> soln. in the presence of Fe, and the titration of Ca<sup>2+</sup> with F<sup>-</sup>. These examples show that in some cases the presence of an extra redox system improves the end-point indication. The advantages of titrations with two indicator electrodes are summarised.

M. J. MAURICE

**4620. Radioassay of finely divided solids by suspension in a gel scintillator.** S. Helf, C. G. White and R. N. Shelley (Explosives and Propellants Lab., Picatinny Arsenal, Dover, N.J., U.S.A.). *Anal. Chem.*, 1960, **32** (2), 238-241.—The counting characteristics of a wide variety of suspended  $\beta$ -emitting radioactive materials in a gel scintillator medium are discussed, and the advantages of suspension over homogeneous soln. counting are illustrated. The radio-elements include <sup>90</sup>Sr, <sup>90</sup>Y, <sup>36</sup>Cl, <sup>22</sup>Na, <sup>132</sup>Ba, <sup>63</sup>Ni, <sup>14</sup>C and <sup>3</sup>H.

K. A. PROCTOR

**4621. Scintillation-bubble chamber.** R. C. Minehart and R. H. Milburn (Lyman Lab. of Physics., Harvard Univ., Cambridge, Mass.). *Rev. Sci. Instrum.*, 1960, **31** (2), 173-174.—A solution of naphthalene (33 g) and PBD phosphor (133 mg) per litre of liquid propane functions as a liquid scintillation counter at temp. of 65° to 75°. This mixture, when expanded in a bubble chamber, gives good tracks for minimum ionising particles and for 100 to 145 Me-V protons. G. SKIRROW

**4622. New correction factor for Geiger-Müller measurements of radioactivity and cosmic radiation.** V. Antonescu and V. Neagu (Univ. Iași). *An. Stiint. Univ. "Al. I. Cuza" din Iași*, 1959, **5** (1), 131-134.—It has previously been shown that spurious counts are often due to internal factors of the tube, but it is now shown that similar false counts can be obtained if the tube is externally earthed. The errors in the case of weak radioactive sources can be as high as 80 to 100%. The plateau of a tube may be foreshortened considerably; sometimes it completely disappears. The slope of the curve is greatly increased. The number of spurious counts increases with the thinness of the glass of the tube, and depends on the amount of surface of the tube which is covered by the metallic earthing foil, which also increases the amplitude of the impulse variation with increase of voltage.

H. SHER

**4623. Radiochemical separations by amalgam exchange.** J. R. DeVoe, C. K. Kim and W. W. Meinke (State Univ., Ann Arbor, Mich., U.S.A.). *Talanta*, 1960, **3** (3), 298-299.—Preliminary results show that an amalgam containing milligram amounts ( $\approx 2\%$ , w/w) of Cd, Tl, Bi, Sr, Zn, In or Pb will remove microgram amounts of the respective radio-isotope from a soln. (2 to 5 M HCl or HClO<sub>4</sub> or 0.5 M NaNO<sub>3</sub>) with a yield  $< 50\%$  after stirring for  $\approx 5$  min. The vol. ratio of soln. to amalgam should be 40:1; Sn and Ga do not exchange.

W. J. BAKER

**4624. A gamma absorptiometer for laboratory analysis of the heavy elements.** W. L. Maddox and M. T. Kelley (Anal. Chem. Div., Oak Ridge Nat. Lab., Tenn., U.S.A.). *Talanta*, 1959, **3** (2), 172-176 (in English).—An instrument constructed in the laboratory for the determination of U or Pu in pure soln. is described and illustrated. The source consists of <sup>241</sup>Am (10 mg) as the trifluoride, cast into a plastic disc. The detector is a thallium-activated scintillating crystal of NaI coupled with a photomultiplier. Circuit diagrams are given. A standard deviation of 0.035 g of U per litre was obtained with a 4.1-cm absorption cell (16 observations).

G. BURGER

**4625. A simple spectrograph for nuclear magnetic resonance.** R. Becherer (Lab. d'Électronique et Radioélectricité de la Sorbonne, B.P. No. 9, Fontenay-aux-Roses, Seine, France). *Compt. Rend.*, 1960, **250** (6), 1037-1039.—The circuitry of a classical spectrograph for nuclear magnetic resonance measurements has been modified and the components geometrically rearranged to increase the signal-to-noise ratio and to reduce in importance the problem of decoupling the emitted and received signals.

E. G. CUMMINS

4626. **High-resolution N.M.R. spectrometer with the radio frequency controlled by the magnetic field.** R. Freeman and R. V. Pound (Nat. Phys. Lab., Teddington, Middlesex). *Rev. Sci. Instrum.*, 1960, **31** (2), 103-106.—The instrument is suitable for the study of high-resolution proton magnetic resonance spectra at a frequency of 30 Mc per sec. Field modulation is imposed in such a way that "side band" responses are observed; this enables lock-in detection to be used, giving increased base-line stability. Spectra are displayed by slowly sweeping the modulation frequency and are thus calibrated directly in frequency. The radio-frequency source is a proton-controlled super-regenerative oscillator whose frequency follows variations of the electro-

magnetic field and so permits relatively low scanning speeds to be used.  
G. SKIRROW

4627. **Mass spectrometer [utilising a thermionic ion source].** United Kingdom Atomic Energy Authority. Brit. Pat. 835,600; date appl. 18.6.46. U.S.A., date appl. 12.6.45.—The mass spectrometer has a thermionic source of positive ions, consisting of a helical filament coated with a compound, e.g.,  $U_2O_3$  or  $UO_2$ , capable of producing the desired positive ions, and a pair of flat, positive focusing electrodes arranged at an angle to each other and spaced relative to the ion source so as to focus the positive ions into a beam directed towards an ion-beam collimator.  
J. M. JACOBS

# ERRATA

January (1960) issue, abstract 149, line 4. *For* Ozman *read* Osman.

May (1960) issue, abstract 1806. The phrases given in parenthesis in lines 7 to 9 and in lines 11 to 12 should be interchanged.

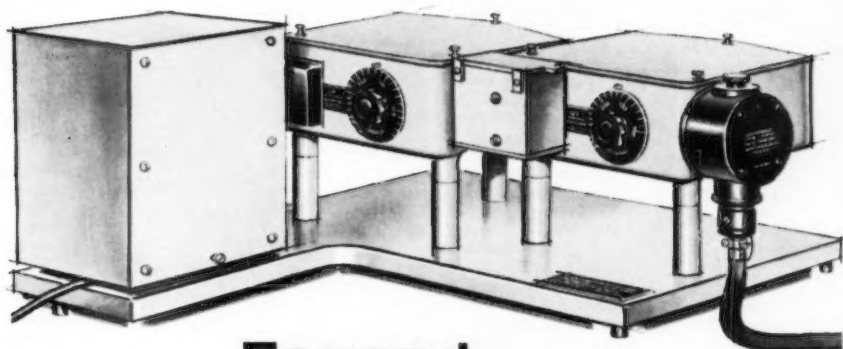
July (1960) issue, abstract 2682, line 11, *For* 52.3 *read* 5.23.

September (1960) issue, abstract 3611, line 2. *For* W. H. Smit *read* W. M. Smit.



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## ABBREVIATIONS

Certain abbreviations in everyday use are not included in the following list. When any doubt might arise from the use of an abbreviation or symbol the word is printed in full.

alternating current	a.c.	milli-equivalent	milli-equiv.
ampere	amp.	milligram	mg
Ångström unit	Å	millilitre	ml
anhydrous	anhyd.	millimetre	mm
approximate, -ly	approx.	millimicrogram	m $\mu$ g
aqueous	aq.	millimolar	mM
atmospher-e, -ic	atm.	millivolt	mV
boiling-point	b.p.	minute (time)	min.
British thermal unit	B.Th.U.	molar (concentration)	M
calorie (large)	kg-cal.	molecul-e, -ar	mol.
calorie (small)	g-cal.	normal (concentration)	N
centimetre	cm	optical rotation	$\alpha_D^t$
coefficient	coeff.	ounce	oz
Colour Index	C.I.	parts per million	p.p.m.
concentrated	conc.	per cent.	%
concentration	concn.	per cent. (vol. in vol.)	% (v/v)
constant	const.	per cent. (wt. in vol.)	% (w/v)
crystalline	} cryst.	per cent. (wt. in wt.)	% (w/w)
crystallised		potential difference	p.d.
cubic	cu.	precipitate (as a noun)	ppt.
current density	c.d.	precipitated	pptd.
cycles per second	c/s	precipitating	pptg.
density	$\rho$	precipitation	pptn.
density, relative	d or wt. per ml	preparation	prep.
dilute	dil.	qualitative, -ly	qual.
direct current	d.c.	quantitative, -ly	quant.
distilled	dist.	recrystallised	recryst.
ethylenediaminetetra-acetic acid	EDTA	refractive index	$n_D^t$
electromotive force	e.m.f.	relative band speed	$R_F$
equivalent	equiv.	relative humidity	r.h.
gram	g	revolutions per minute	r.p.m.
gram-molecule	mole	saponification value	sap. val.
half-wave potential	$E_{\frac{1}{2}}$	saturated calomel electrode	S.C.E.
hour	hr.	second (time)	sec.
hydrogen ion exponent	pH	soluble	sol.
infra-red	i.r.	solution	soln.
insoluble	insol.	specific gravity	sp. gr.
international unit	i.u.	specific rotation	$[\alpha]_D^t$
kilogram	kg	square centimetre	sq. cm
kilovolt	kV	standard temp. and pressure	s.t.p.
kilowatt	kW	temperature	temp.
liquid	liq.	ultra-violet	u.v.
maxim-um, -a	max.	vapour density	v.d.
melting-point	m.p.	vapour pressure	v.p.
microgram	$\mu$ g (not $\gamma$ )	volt	V
microlitre	$\mu$ l	volume	vol.
micromole	$\mu$ mole	watt	W
micron	$\mu$	wavelength	$\lambda$
milliampere	mA	weight	wt.

In addition, the following symbols may be used in conjunction with numerical values or in mathematical expressions—

greater than	>	less than	<
not greater than	$\nlessgtr$	not less than	$\ngtrless$
is proportional to	$\propto$	of the order of, approximately	$\approx$

The principal Pharmacopoeias are denoted by B.P., U.S.P. or D.A.B., together with the identifying roman numeral or year.

Valency states are represented by a superscript roman numeral, e.g., Fe<sup>II</sup>, Mo<sup>V</sup>. Substances in the ionic state are represented by Na<sup>+</sup>, Fe<sup>3+</sup>, Fe<sup>2+</sup>, etc., for cations and by Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, PO<sub>4</sub><sup>3-</sup>, etc. for anions.

## ANALYTICAL ABSTRACTS

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## CONTENTS

	Abstract
<b>General Analytical Chemistry</b>	
Reviews; reagents; methods of general application .. .. .	4090
<b>Inorganic Analysis</b>	
General methods; elements (in order of the Periodic Table); minerals; industrial products .. .. .	4107
<b>Organic Analysis</b>	
Elements and radicals; organic compounds; industrial products .. .. .	4296
<b>Biochemistry</b>	
BIOLOGICAL FLUIDS; ANIMAL AND VEGETABLE TISSUES .. .. .	4394
PHARMACEUTICAL ANALYSIS .. .. .	4446
<b>FOOD</b>	
Food additives; beverages; edible oils and fats; vitamins .. .. .	4471
<b>SANITATION</b>	
Air; water; sewage; industrial wastes .. .. .	4508
<b>AGRICULTURAL ANALYSIS</b>	
Soil; fertilisers; herbicides; pesticides; animal feeding-stuffs .. .. .	4520
<b>General Technique and Apparatus</b>	
GENERAL .. .. .	4540
CHROMATOGRAPHY; ION EXCHANGE; ELECTROPHORESIS .. .. .	4556
OPTICAL .. .. .	4571
THERMAL .. .. .	4589
ELECTRICAL .. .. .	4591

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